

Nitrogen and Phosphorus Reactions in
Overland Flow of Wastewater

Louisiana State Univ.
Baton Rouge

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August 1981

NITROGEN AND PHOSPHORUS REACTIONS IN OVERLAND
FLOW OF WASTEWATER

by

R. A. Khalid, I. C. R. Holford, M. N. Mixon
and W. H. Patrick, Jr.

Laboratory for Wetland Soils and Sediments
Center for Wetland Resources
Louisiana State University
Baton Rouge, Louisiana 70803

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Project Officer

Bert E. Bledsoe
Wastewater Management Branch
Robert S. Kerr Environmental Research Laboratory
Ada, Oklahoma 74820

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FOREWORD

The U.S. Environmental Protection Agency was established to coordinate the administration of major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques, and new technologies through which optimum use of the Nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

The U.S. Environmental Protection Agency's Office of Research and Development conducts this search through a Nationwide network of research facilities. As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs including the development and demonstration of soil and other natural systems for the treatment and management of municipal wastewaters.

The overland flow treatment process for land treatment of municipal wastewaters uses the varying biological, physical, and chemical processes that occur on or near the surface of a vegetated gently sloping terrace to treat the wastewater as it flows from the top to toe where it is collected for surface discharge. This is a three-year study into the basic mechanisms and reactions, that occur in an overland flow system, which determines the fate of nitrogen and phosphorus species in wastewater. The study was conducted using simulated wastewaters to control the species of nitrogen and energy source. Results of this study provide information on the soil-plant relationship and the ultimate fate of nutrients in this type of treatment system.

This report contributes to the knowledge which is essential for the U.S. Environmental Protection Agency to meet requirements of environmental laws and enforce pollution control standards which are reasonable, cost effective, and provide adequate protection for the American public.

Clinton W. Hall

Clinton W. Hall
Director

Robert S. Kerr Environmental Research Laboratory

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ABSTRACT

Biochemical transformations of labelled ammonium-nitrogen resulting from the overland flow treatment of simulated wastewater were studied in small scale test models established with vegetated soils. The contribution of gaseous nitrogen loss in the removal of simulated wastewater nitrogen was also studied in the sealed growth chambers. The results of overland flow experiments indicated the existence of aerobic-anaerobic zones in the soil mass to facilitate nitrification-denitrification processes and enhance nitrogen losses to the atmosphere. The incomplete nitrification of ammonium-nitrogen in the simulated wastewater applied to overland flow models in Mhoon and Olivier soils and that applied to Grenada soil in the growth chamber studies simulating overland flow environment suggests that nitrification reactions may be limiting the proportion of nitrate-nitrogen available for denitrification reactions. The loss of applied ammonium-nitrogen attributed to denitrification reactions in the overland flow experiments ranged from 3 to 35%. In the growth chamber studies where alternate aerobic-anaerobic conditions were maintained with controlled soil moisture, loss was as high as 59%. The lack of nitrate accumulation in the soil mass indicated that denitrification process was not limiting the gaseous loss of applied nitrogen. The rate of nitrogen loss in the nitrate treatments was about two orders of magnitude greater than in the ammonium treatments, and followed a zero order reaction. The plant uptake of nitrogen in the overland flow and growth chamber studies accounted for 23 to 62% of applied ammonium-nitrogen and thus resulted in the maximum removal of wastewater nitrogen compared to other chemical and biochemical processes. About 5% of applied ammonium was lost through ammonia volatilization in the studies. The results of the research show that plant uptake, nitrification-denitrification reactions and ammonia volatilization were all important processes that should be maximized for an efficient removal of municipal wastewater nitrogen in overland flow treatment systems.

The mechanisms of phosphorus sorption and desorption were investigated under both laboratory and overland flow conditions. Laboratory studies were conducted to determine the effects of changes in redox potential, pH, and the duration of anaerobiosis and re-oxidation on phosphorus sorption and mobility in soil suspensions. An overland flow experiment was performed to determine the influence of prereduced soil conditions and pH amendment

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on the removal of phosphorus-32 applied in simulated wastewater. The results of laboratory studies indicated that initial flooding of aerated soil for about 3 weeks was accompanied by a large increase in phosphorus sorption capacity and decrease in phosphorus mobility. Longer periods of flooding, however, would cause a marked decrease in phosphorus sorption capacity and a corresponding increase in phosphorus mobility and leaching losses in acid soils. Calcium phosphate precipitation under alkaline soil conditions increased phosphorus sorption capacity of soils. The results of the overland flow experiment also demonstrated that the efficiency of phosphorus removal from municipal wastewater was greatly enhanced by lime addition to the soil compared to nonlimed flooded soil. The phosphorus sorption isotherms determined in the laboratory and the sorption parameters computed by the Langmuir "two surface" equation demonstrated that the efficiency of phosphorus removal in the overland flow experiment was related to the phosphorus sorption capacity of various treatments.

This report was submitted in fulfillment of Grant No. R 803612 by Louisiana State University under the sponsorship of U.S. Environmental Protection Agency. This report covers the period April 14, 1975 to June 14, 1979 and work was completed as of July 31, 1979.

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SECTION 1

INTRODUCTION

The implementation of Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) has been a driving force in the development of land application as a major management alternative for the effective treatment of municipal wastewater. This has resulted in a renewed interest in studying the various processes involved in the removal of pollutants in various land treatment systems. The three major types of land treatment systems recognized in the United States and elsewhere include slow rate, rapid infiltration, and overland flow application. The land requirements, design characteristics, soil properties and hydraulic loadings for these treatment systems are discussed in detail in a recent U. S. Environmental Protection Agency (EPA) Manual (EPA, 1977).

Most municipal wastewaters contain significant concentrations of nutrients, primarily nitrogen and phosphorus. Both nitrogen and phosphorus can be serious pollutants if discharged to surface waters. Overland flow, also called grass filtration, has been shown to be an effective treatment system for removal of nitrogen from municipal wastewater while phosphorus removal efficiency has been found to vary over a wide range (Hoeppe et al., 1974; Carlson et al., 1974; Thomas et al., 1976; Lee and Peters, 1978). The U. S. EPA has undertaken a comprehensive research program dealing with loading rates for different soil types, frequency of application for maximum nutrient removal, mechanisms involved in transformations, retention, and movement in the soil, and management practices for controlling nitrogen and phosphorus behavior in an overland flow treatment system. The present investigation funded by EPA was focused on the mechanisms of various nitrogen and phosphorus removal processes in an overland flow treatment model. The understanding of these processes will aid in designing overland flow facilities for a more efficient and economical treatment of municipal wastewater which would minimize nutrient loading in the receiving surface and ground waters.

The specific objectives of this research investigation were:

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1. To investigate the distribution of applied simulated wastewater in the various components of overland flow treatment system.

2. To evaluate the role of nitrification-denitrification reactions, ammonia volatilization, plant uptake and immobilization in nitrogen removal in small scale overland flow treatment systems.

3. To measure the effects of controlled oxidation-reduction conditions and pH changes on phosphorus sorption and mobility in a soil suspension.

4. To determine the effects of prereduced soil conditions and lime application on the efficiency of soil-plant system in the removal of phosphorus in an overland flow treatment model.

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Several controlled laboratory and small scale overland flow experiments were conducted to determine the mechanisms of nitrogen and phosphorus removal processes from simulated wastewater during overland application. Crowley, Olivier, Mhoon and Granada soils and rye grass, Bermuda grass and rice plants were used in the various experiments. Overland flow test models, 30 centimeters (cm) width, 152 cm length and 13 cm depth, were used to study the distribution of applied water into various system components. The results were fitted into a mathematical model to predict the behavior of water movement under field conditions.

Similar overland flow test models were used to investigate the fate of applied labelled nitrogen in an established soil-plant system. Measurements of gaseous nitrogen losses were made in the sealed overland flow test models and other growth chamber studies.

The mechanisms of phosphorus sorption and desorption were investigated under both laboratory and simulated overland flow conditions. Laboratory studies were conducted to determine the effects of changes in redox potential, pH, and the duration of anaerobiosis and re-oxidation on phosphorus sorption and mobility in soil suspensions. An overland flow experiment was performed to determine the influence of prereduced soil conditions and pH amendment on the removal of phosphorus-32 applied in simulated wastewater.

The results of controlled laboratory and small scale overland flow experiments with simulated wastewater containing nitrogen and phosphorus that may be significant in the land application of municipal wastewater are as follows:

WATER MOVEMENT

1. The recovery of simulated wastewater effluent in the runoff fraction in the small scale overland flow experiments ranged from 50 to 60% of applied water. The fraction of applied water collected in the subflow was 9 to 23%. The effect of varying slope from 1.1 to 4.4% on the flow rate of simulated wastewater was not

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significant in the small scale overland flow model with growing plants.

2. The water movement in the overland flow system as computed by the non-steady flow model was primarily controlled by the application rate, the friction slope, the hydraulic characteristics of the soils, the evapotranspiration and the slope angle.

NITROGEN REACTIONS

1. The existence of well oxidized soil conditions in the surface soil and of well oxidized to reduced conditions in the subsurface soil was indicative of the occurrence of simultaneous nitrification and denitrification reactions in the overland flow experiments and hence nitrogen loss to the atmosphere.

2. Low soil pH in the range of 5.1 to 6.0 and lack of an easily-available energy source resulted in negligible losses of applied ammonium-nitrogen through nitrification-denitrification reactions in the overland flow model.

3. The loss of ammonium-nitrogen through ammonia volatilization reactions in the overland flow experiments and sealed growth chamber studies accounted for about 5% of total nitrogen added. The pH of soils used in various ammonia volatilization studies ranged from 6.4 to 7.6 and would therefore explain the relatively small losses of applied ammonium through ammonia volatilization reactions. Published literature suggests that in more alkaline soil conditions ammonia volatilization losses would be appreciable.

4. The movement of ammonium-nitrogen in the simulated wastewater applied to the overland flow model was restricted to the upper end of the slope. Most of the residual ammonium-nitrogen recovered at the end of overland flow experiments was present in the top few centimeters of soil mass. More nitrate-nitrogen had moved downslope and in the subsurface soil compared to ammonium-nitrogen.

5. The loss of applied ammonium-nitrogen attributed to denitrification reactions in the overland flow experiments ranged from 2.9 to 35.4%. In the growth chamber studies where alternate oxidized and reduced soil conditions were attained with controlled soil water content, loss of applied ammonium-nitrogen was as high as 59%. No significant accumulation of nitrate-nitrogen in the soil mass occurred which indicated that the denitrification process was not a limiting factor in the gaseous loss of applied nitrogen.

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6. The plant uptake of nitrogen in the overland flow and growth chamber studies accounted for 23 to 62% of applied ammonium-nitrogen and thus resulted in the maximum removal of wastewater nitrogen compared to other chemical and biochemical processes. Also, preferential uptake by rye grass plants of ammonium-nitrogen over nitrate-nitrogen was demonstrated in the study.

7. The effect of rhizosphere on the denitrification loss of applied nitrogen in the overland flow experiment was not significantly different from the system in which no plants were growing.

The results of the experiments suggest that the gaseous loss of applied nitrogen can be maximized during land application of wastewater if conditions favorable for simultaneous nitrification-denitrification reactions are attained through careful manipulation of soil-plant systems. Some of the important factors that control these reactions are redox potential, pH, readily available carbon source and large population of appropriate microbes. Any overland flow treatment facilities aimed at maximizing nitrogen loss must optimize these variables. Plant uptake of wastewater nitrogen during overland flow application accounts for a large fraction of nitrogen removed. More research need to be conducted on the selection of plant species that have affinity for greater nitrogen accumulation and that can be harvested often to maximize nitrogen removal. Wherever economically feasible, lime additions with the wastewater application may be made to enhance ammonia volatilization losses of applied ammonium-nitrogen.

PHOSPHORUS REACTIONS

Laboratory Studies

Applicable to Acid Soils--

1. After about 20 days of continuous flooding there was a very large increase in sorption capacity and decrease in leaching losses from wastewater additions containing more than five micrograms phosphorus/milliliter (μg phosphorus/ml). However, from more dilute wastewater there may be a slight increase in leaching losses compared with those from aerated soil.

2. Longer periods of flooding (more than 40 days) caused a gradual decrease in phosphorus sorption capacity and a corresponding increase in phosphorus mobility and leaching losses.

3. Re-oxidation for periods up to 30 days caused a marked decrease in phosphorus sorption capacity, and leaching losses from previously applied wastewater would be moderately greater than from wastewater applied to aerated soil.

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Applicable to Non Acid Soils--

4. Phosphorus sorption capacity increased immediately by the addition of calcium in the wastewater, causing an increase in calcium phosphate precipitation.

5. With increasing reduction, pH fell to near neutral causing a decrease in the negative charge of the iron oxide surfaces and an increase in the solubility of calcium phosphates. Consequently, phosphorus sorption by calcium phosphate precipitation will decrease but the bonding energy of the iron oxide surfaces will increase. The net effect of these changes would be some increase in sorption capacity and a larger increase in buffer capacity so that leaching losses would be smaller than from an aerated soil.

6. Re-oxidation would reverse the changes in pH and buffer capacity so that the phosphorus sorption capacity and leaching losses would be similar to those of an aerated soil.

Requirements for Further Laboratory Research--

1. Because of the importance of soil pH and reducible iron content, further research needs to be performed on a range of soils varying in pH and reducible iron content.

2. Short-term kinetic studies of phosphorus sorption are important because adsorption and precipitation are fast reactions. However, the kinetics of anaerobic changes, such as pH and iron chemistry, which affect subsequent phosphorus sorption and mobility, require further study. Longterm kinetic studies of phosphorus sorption due to occlusion in hydrous oxide crystals and organic incorporation also require further research.

3. Experimental evidence suggests that re-oxidation of soils can reverse the beneficial effects of reduction on phosphorus sorption capacity and mobility. Further long-term studies are required to optimize management strategies for the duration of wastewater application and reaeration intervals.

Overland Flow Experiment

1. The results of overland flow experiments conducted on Crowley silt loam-rye grass system established at 1.2% slope demonstrate that the efficiency of phosphorus removal from municipal wastewater would be greatly enhanced by addition of lime (calcium carbonate) to the soil. The prereduction of soil-plant system for extended period of time may also result in more phosphorus removal than less-reduced non-limed soil.

2. The phosphorus sorption isotherms conducted in the laboratory on the pretreated soils and the sorption parameters computation by the Langmuir "two surface" equation demonstrated

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that the efficiency of phosphorus removal in the overland flow experiment was related to the phosphorus sorption capacity of various treatments.

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A slightly higher desorption of phosphorus sorbed in the overland flow as well as laboratory studies in the limed treatments was due to the lower phosphorus bonding energy in this treatment. Phosphorus sorbed under alkaline conditions was more available to growing plants than the unamended treatments.

The results of this study also suggest that phosphorus sorption is a kinetic process and that the leaching losses of phosphorus retained by the soil mass during overland flow application would be smaller due to longer reaction time as compared to the desorption potential determined in the laboratory.

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SECTION 3

DISTRIBUTION OF APPLIED WASTEWATER IN SOIL-PLANT SYSTEM IN AN OVERLAND FLOW TREATMENT MODEL

INTRODUCTION

The water in the sewage effluent is considered to be a transporting medium of various constituents which interact with the treatment system through physical, chemical and biological processes. In the overland flow treatment system, wastewater is applied over the upper reaches of a sloped land area. Renovation is accomplished as the wastewater flows through the vegetated surface down the slope. Most of the wastewater flows over the surface and is collected as runoff at the end of the slope. The remainder percolates into the soil and forms soil water flow referred to as subflow and is collected at the bottom of the slope. In addition to these two modes of water movement, evapotranspiration may also constitute a significant fraction of applied wastewater lost from the system. The objective of the experiments reported in this section were:

1. To study the relative distribution of added influent in the runoff and subflow effluent and that retained by the soil-plant system in an overland treatment model.
2. To investigate the effects of varying slope on the relative distribution of applied water into various components stated in (1).
3. To obtain a quantitative understanding of the mechanism of water movement by using a mathematical model that would accurately predict water movement in the overland flow treatment system.

MATERIALS AND METHODS

Construction of Overland Flow Test Model

The containers for the test model were constructed of a 1.27-cm thickness of plywood with inside dimensions of 30-cm in width by 152-cm in length by 13-cm in depth. Two holes were drilled in the lower end of the container on one side for

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collecting subflow. A plexiglass port was attached on the same end to collect runoff. The interior of the constructed model was coated with an epoxy paint and lined with a six mil polyethylene sheeting to prevent water seepage or contamination from the construction material.

Experimental Procedures

In the test containers described above, 62 kilograms (kg) of air-dried Mhoon silt loam soil was uniformly packed with 5-cm increments at a time. Total height of soil mass in the test containers ranged from 11.0 to 11.5 cm. The soil was then saturated with water, allowed to dry and was repacked. A schematic diagram of the test model is given in Figure 1.

The test container was planted with rye grass (*Lolium perenne*, L.) at a seed rate of 20 grams/square meter (g m^{-2}). Tap water was sprinkled regularly as needed for normal plant growth. When rye grass was grown to a height of over 30 cm the test container was put on top of a table on a 2% slope in a room fitted with a combination of fluorescent and incandescent lights. A 12-hour light-dark cycle was maintained to provide a normal growth cycle. Water was pumped in at the upslope end with a peristaltic tube pump and distributed through a paper towel folded across the width of the test container. The volume of the water, equivalent to a 2-cm depth, and amounting to 9.3 liters, was applied in a five-hour period at an average input rate of 30 milliliters/minute (ml/minute). The water was applied every day for a few days without recording the runoff and subflow. The purpose was to check the pattern of downslope flow through the soil-grass system, to check for any abnormalities in the system, and to bring the soil to a uniform moisture level before measuring water in the runoff and subflow.

For the collection of data, 9.3 liters of water was applied every day for three consecutive days and the volume collected in the runoff and subflow at different time intervals was recorded. No water was applied on the fourth day. This was followed by three more days of water application with runoff and subflow recorded daily.

Using the same soil-grass system another experiment was conducted to investigate the effects of varying slope on the relative distribution of applied water into various components.

Mathematical Computations

An approximate analytical solution to the water flow in an overland flow system was computed, based on the shallow water equation of Chen and Chow (1971) and the non-steady soil water flow equation of Nakano (1978). The computer programming and

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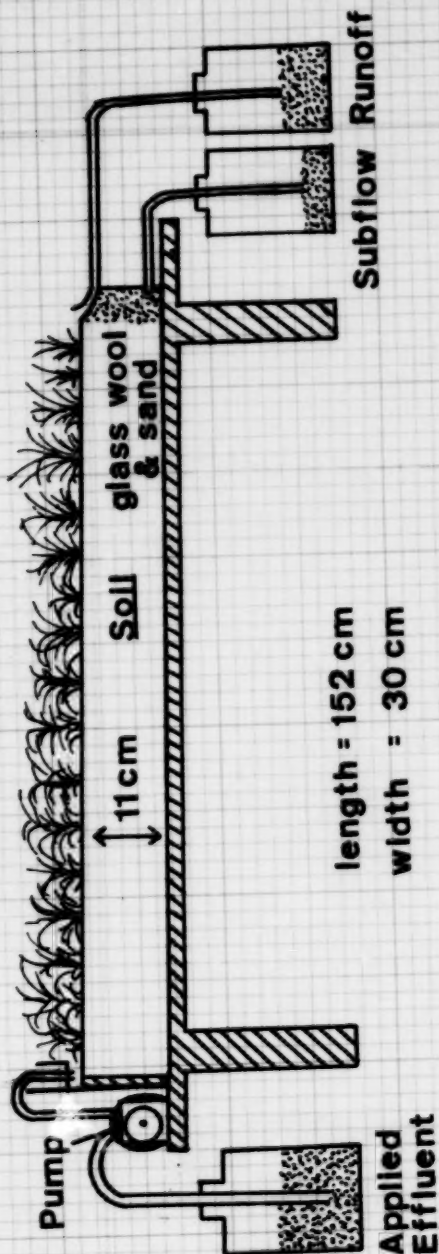


Figure 1. Longitudinal section of the overland flow wastewater treatment model.

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data computations for the comparison of experimental and theoretical water flow values were performed by Dr. Y. Nakano of U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire. Details of the mathematical computations, solution of equation and appropriate boundary conditions are documented elsewhere (Nakano, Khalid and Patrick, 1978) and will not be presented here.

RESULTS AND DISCUSSION

Distribution of Applied Water in an Overland Flow Model

From the data presented in Table A-1, the following observations may be made, related to the flow pattern of water applied to a soil-grass system placed on a 2% slope.

1. The elapsed time between the start of overland flow application at the upslope and draining at the downslope ranged from 13 to 30 minutes. A one-day break between the third and fifth day did not alter the runoff flow pattern.

2. Thirty to sixty minutes elapsed before the subflow began dripping from the test container at the downslope. It should be stated that when water was applied on the fifth day after one-day break in water application, actual subflow drainage time was longer. It is likely that this increase in retention time was caused by loss of water through evapotranspiration since the soil was drier at the beginning of the fifth day. Because of this, comparatively more water was retained by the soil than on the third day of water application.

3. The outflow of applied water collected in the runoff and subflow became constant after two to three hours and generally maintained that flow rate until the entire volume of water was depleted.

4. The flow rate in the runoff decreased from over 20 ml/minute to less than one ml/minute within 20 minutes after the pump was turned off. The decrease in subflow was comparatively more gradual, and it took a longer time for the subflow to stop flowing from the test container.

The total volume of water recovered in the runoff and subflow was recorded daily. The difference between the total amount added and that recovered in the runoff and subflow was designated as lost through evapotranspiration, and retained by the soil to replenish for the loss of water from the soil-plant system during the previous 18 to 20 hours. The data summarized in Table 1 indicate that 50 to 66% of the total water applied was recovered in the surface runoff. The fraction of applied water collected

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TABLE 1. DISTRIBUTION OF WATER APPLIED TO A MOON SOIL-RYE GRASS SYSTEM IN AN OVERLAND FLOW TEST MODEL ADJUSTED TO 2.2% SLOPE

Days water applied	Volume applied, l	Flow rate ml/minute	Fraction recovered, %	
			overland flow	subflow balance**
1	9.3	28.9	54.6	22.9
2	9.3	27.4	51.5	22.7
3	9.3	25.6	59.2	14.6
No water was applied on the 4th day				
5	9.3	32.6	50.2	9.3
6	9.3	32.0	67.1	9.2
7	9.3	32.1	65.9	11.7
				22.3

* Rye grass in the test model was 60 days old on the 1st day of water application.

** Balance includes water lost through evapotranspiration and that retained by the soil.

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in the subflow ranged from 9 to 23%. Twenty-two to 40% of applied water was utilized by soil and the plants.

Influence of Varying Slope

Using the same soil-grass system, a study was conducted to investigate the effect of varying the slope on the relative distribution of applied water into various components. The data presented in Table 2 and Table A-2 show that an increase in slope from 1 to 4% resulted in proportionately more runoff and less subflow and soil retention. The elapsed time between the start of water application, and the outflow in the runoff and subflow also decreased. However, the flow rate of runoff and subflow with time was identical for four different slopes under study as illustrated in Figure 2.

The data presented in Figure 2 and Table 2 indicate that the main effect of slope was on runoff. An increase in slope shortened the time duration of the unsteady state at the start and end of application and did not increase the rate of runoff in the steady state. This may also suggest that the effect of slope on the flow rate and hence on the retention of nutrients from the water may not be significant in the steady state period in the small scale soil-plant systems.

Comparison of Experimental Data and Mathematical Computations of Water Flow in Overland Flow Model

The data plotted in Figure 2 indicated that a gradual increase in slope from 1.1 to 4.4% resulted in proportionately more runoff and less subflow recovered. The increase of slope, therefore, tends to shorten the time duration of the non-steady state of overland flow at the start and end of application, but does not have as much effect on soil water flow. As a result of this prolonged steady state of overland flow, proportionately more runoff and less subflow were recovered.

This phenomenon of water movement in the overland flow model as a function of slope was computed from a set of shallow water equations and soil water equations. The shallow water equations (Chen and Chow, 1971) are used as a first approximation to non-steady overland flow. The equations, in the two dimensional Cartesian coordinate system (Figure 3), are

$$\frac{\partial h}{\partial t} + \frac{\partial (uh)}{\partial x} = (q - I - E) \cos \alpha \quad (1)$$

and

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + g \cos \alpha \frac{\partial h}{\partial x} = g(\sin \alpha - S_f) \frac{qu}{h} \quad (2)$$

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TABLE 2. THE EFFECT OF SLOPE ON THE DISTRIBUTION OF WATER APPLIED TO A MHOON
SOIL-RYE GRASS SYSTEM IN AN OVERLAND FLOW TEST MODEL

Slope %	Volume applied l	Flow rate ml/minute	Fraction recovered, %		Time, minutes	
			runoff	subflow evapotranspiration + soil retention	runoff	subflow started
1.1	9.3	30.4	55.3	16.5	23	55
2.2	9.3	29.9	60.7	16.7	17	21
3.3	9.3	29.5	72.7	5.5	13	23
4.4	9.3	28.1	69.6	11.0	14	24

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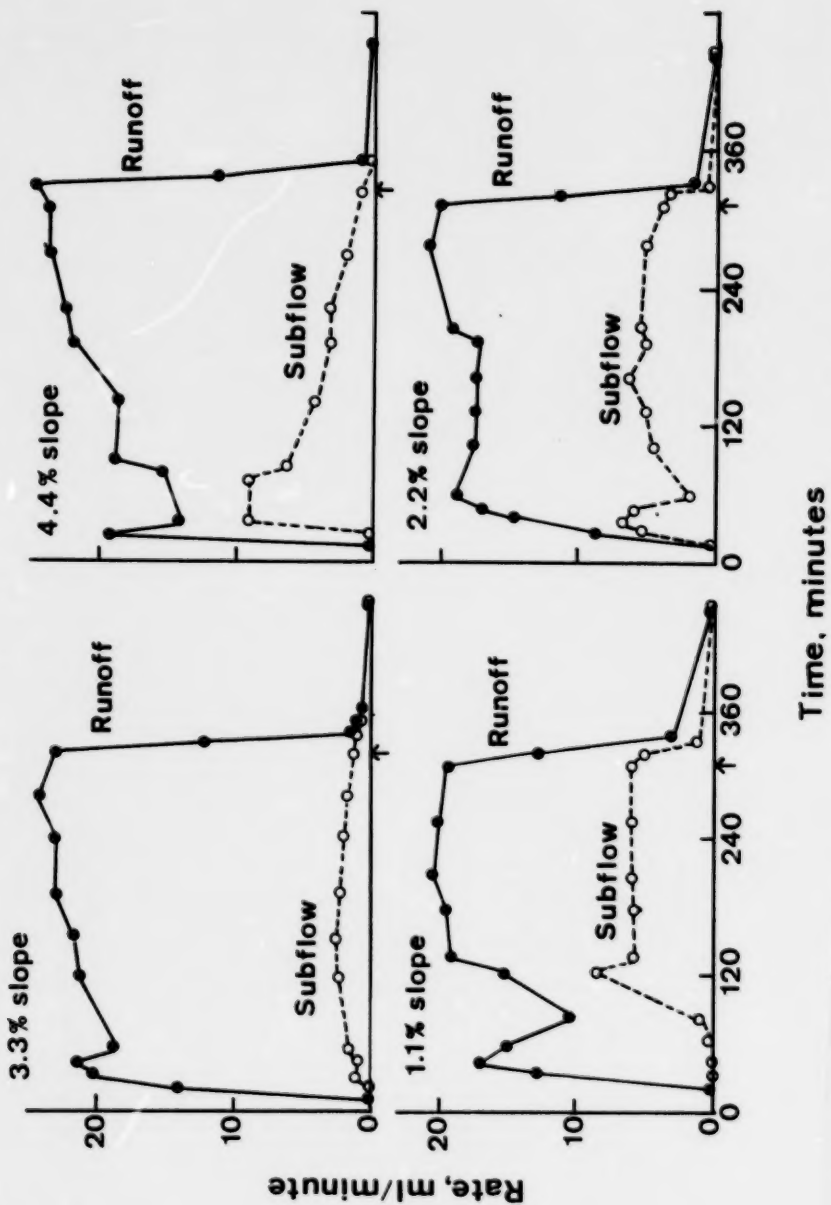


Figure 2. The effect of slope on the rate of runoff and subflow in Mhoon soil-rye grass system $\uparrow$ = Time total volume pumped.

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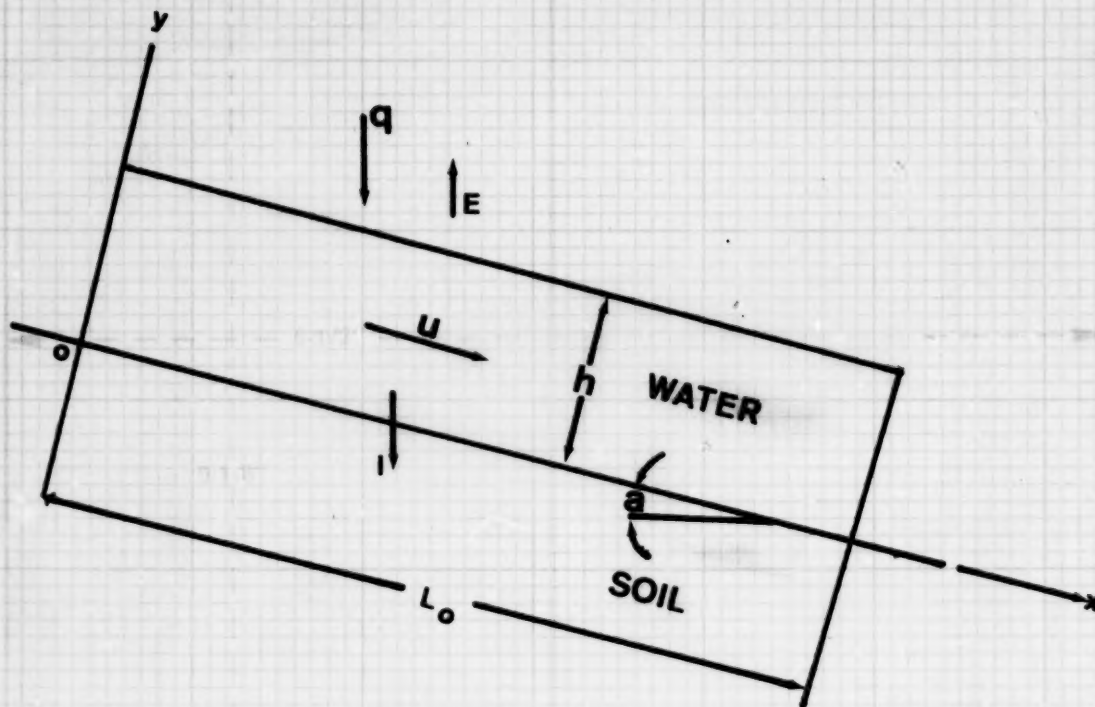


Figure 3. Coordinate system (x,y) used in Equations (1) and (2).

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where h = depth of flow, measured in the y direction [cm]
 t = time [s];
 u = average velocity over the cross section in the direction of x axis [cm/s];
 x = distance [cm];
 q = lateral inflow, rain and wastewater [cm/s];
 I = infiltration rate [cm/s];
 E = evaporation from the surface [cm/s];
 α = slope angle [radian];
 g = acceleration of gravity = 980.6 [cm/s²];
 S_f = friction slope [-].

The soil water equation of Nakano (1978), used to describe the balance of soil water in the two dimensional coordinate system (x, z) (Figures 4 a, b) in the overland flow model is as follows:

$$\beta \frac{\partial \epsilon h}{\partial t} = \frac{\partial}{\partial x} k(h) \frac{\partial h}{\partial x} + (1 + \gamma^2) \frac{\partial}{\partial z} k(h) \frac{\partial h}{\partial z} - \frac{\partial k(h)}{\partial z} - \gamma \left[\frac{\partial}{\partial x} k(h) \frac{\partial h}{\partial z} + \frac{\partial}{\partial z} k(h) \frac{\partial h}{\partial x} \right] - \lambda \quad (3)$$

where $\beta(h) = d\theta/dh$ is the differential liquid capacity, and θ is the volumetric water content;
 h = pressure head [cm H₂O];
 k = hydraulic conductivity [cm/s];
 λ = sink term to simulate removal of water by plants;
 ϵ = linear function of h and defines the thickness of the artificial transitional zone.
 $\gamma = \tan \alpha$

The two computer programs, one for non-steady shallow-water flow (Equations 1, and 2), and one for non-steady soil water flow (Equation 3) were combined to test the fitness of the analytical solution to the experimental water flow data presented in Table A-2. The details of the computer simulations and the initial and boundary conditions are presented elsewhere (Nakano, Khalid and Patrick, 1978).

The results of the computations are shown in Figure 5 (a) to (d). The computed rate of the total water recovered agrees well with the experimental data, but the computed rate of subflow does not. This discrepancy could be attributed to the difficulty in the experimental determination of the relative proportional of runoff and subflow. It is possible that some physical processes that may influence water movement in the system were overlooked.

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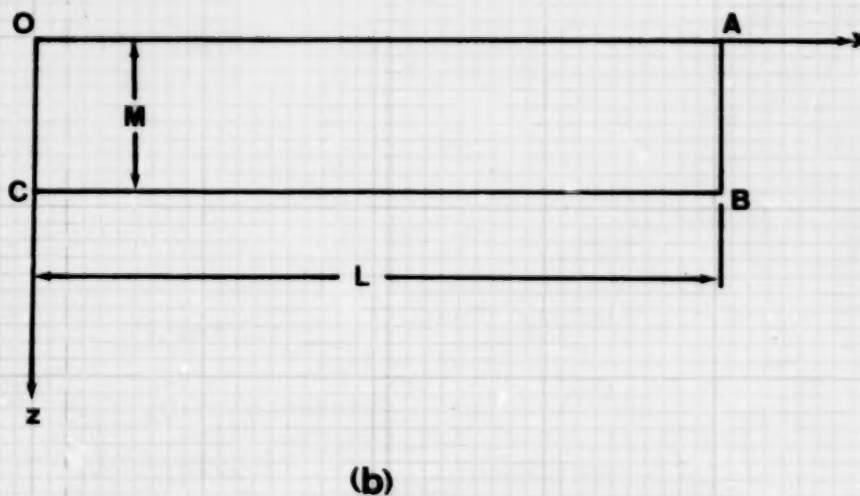
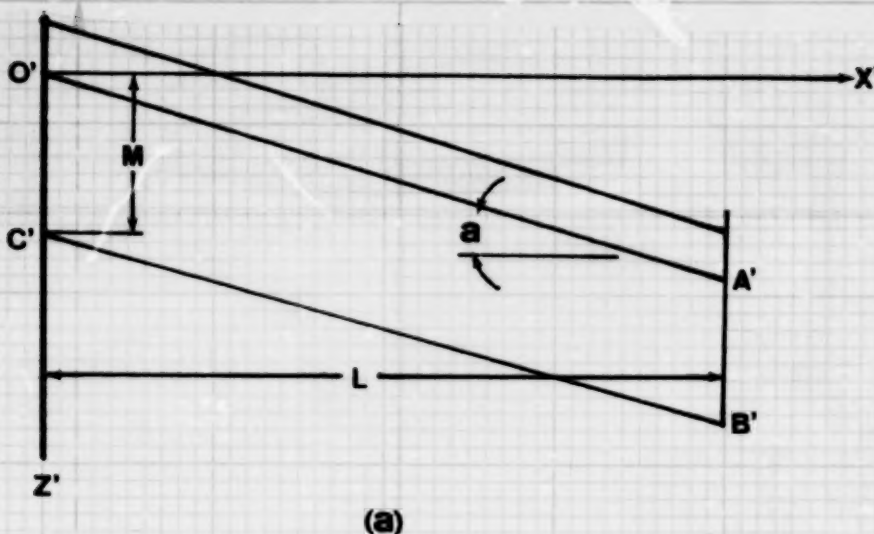


Figure 4. (a) Two dimensional cartesian coordinate system (x,z) used in Equation 3.
(b) Two dimensional coordinate system (x,z) used in Equation 3.

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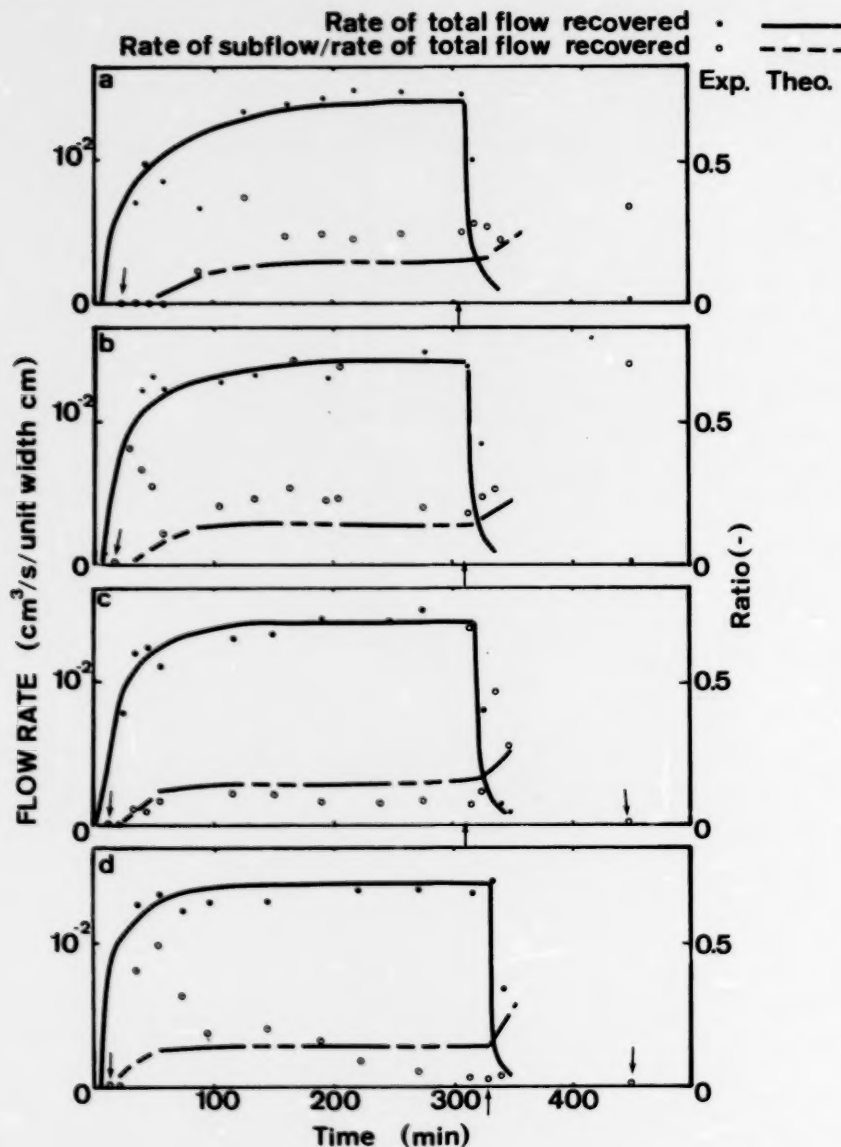


Figure 5. Comparison between the experimental data in Table A-2 and the results of computations (a) 1.1% slope; (b) 2.2% slope; (c) 3.3% slope; (d) 4.4% slope.

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The results of these computations and the comparison with the experimental data suggest that the water movement in the system was primarily controlled by the application rate, the friction slope, the slope angle, the hydraulic characteristics of soils, and the evapotranspiration. The computer simulation of non-steady flow satisfactorily predicts the rate of total water recovered. An understanding of the physical processes may be an important first step to obtain quantitative information on the mechanisms of chemical and biological processes in the overland flow treatment system of wastewater containing pollutants.

CONCLUSIONS

The results obtained from this study indicate that 50 to 66% of the total water applied to the overland flow system was recovered in the surface runoff. The fraction of applied water collected in the subflow was 9 to 23%. The remaining 22 to 40% of applied water was retained by the soil or lost through evapotranspiration. The results also suggest that the effect of varying slope (from 1.1 to 4.4%) on the flow rate and hence on the retention of nutrients from the wastewater may not be significant in the small scale soil-plant systems. The computer simulation of non-steady flow satisfactorily predicted the rate of the total water recovered. The water movement in the overland flow system was primarily controlled by the application rate, the friction slope, the hydraulic characteristics of soils, the evapotranspiration and the slope angle.

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SECTION 4

NITROGEN REMOVAL PROCESSES IN OVERLAND FLOW TREATMENT
OF WASTEWATER

INTRODUCTION

Many processes have been proposed in the literature for the removal of nitrogen from wastewater and polluted streams. The principal nitrogen control methods that are suggested as practical include ammonia stripping, ion exchange, breakpoint chlorination, electrochemical treatment, biological nitrification-denitrification and land application (Reeves, 1972; EPA, 1975; Sutton, Murphy and Dawson, 1975). Where feasible, land application has been suggested as an effective, low cost method for advanced treatment of wastewater (Carlson, Hunt and Delaney, 1974). This is usually accomplished by designing overland flow treatment facilities where wastewater is applied to the soil-plant system at a gentle slope. The major physical, chemical, and biological mechanisms involved in the removal of wastewater nitrogen in land application through overland flow include physical adsorption of ammonium-nitrogen by the soil exchange complex, ammonia volatilization, immobilization of ammonium- and nitrate-nitrogen by soil microbes and organic matter, biological denitrification reactions and plant uptake.

The overland flow treatment of wastewater produces conditions similar to that occurring in rice soils under flooded conditions, and has a profound effect on normal soil processes. For example, the slow diffusion of oxygen through the water results in the development of a thin oxidized layer, which is characterized by a high oxidation-reduction (redox) potential and a high content of the oxidized form of nitrogen such as nitrate and nitrite. Below this oxidized layer, the absence of oxygen also results in a reduced zone characterized by low redox potential, the presence of reduced products such as ammonium, nitrous oxides, nitrogen gas, and the products of anaerobic decomposition of organic matter. Thus, both oxidation and reduction processes will be occurring in overland flow treatment of wastewater. Oxidized conditions favor conversion of applied ammonium to nitrate (nitrification), which may leach to the lower anaerobic layer or be taken up by plants. In the absence of oxygen, gaseous nitrogen losses of nitrate (denitrification) and nitrogen mineralization releasing free ammonium are favored. The transformation of gaseous and ammonium-nitrogen to organic amino acids

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and proteins (nitrogen fixation) is also accelerated by reduced soil conditions. The presence of both oxidized and reduced conditions which may decrease levels of soluble nitrogen are thus of great benefit for the tertiary treatment of wastewater by land application.

Some work has been conducted in recent years on the characterization of aerobic and anaerobic zones and the nitrogen transformation reactions. The thickness of the aerobic layer is reported to generally vary from a few millimeters in soils of high biological activity where there is greater demand for oxygen to one or two cm in soils of low biological activity, where there is less demand for oxygen (Patrick and DeLaune, 1972; Engler and Patrick, 1974; Reddy et al., 1976). The presence of this surface aerobic layer in flooded soil conditions is of great ecological importance because it acts as a sink for plant nutrients (Armstrong, 1965; Mortimer, 1971; Fitzgerald, 1969). Concentration of oxygen over the flooded soil, the amount of ammonium-nitrogen in the floodwater, and the accumulation of nitrate in the surface layer strongly influence the thickness of the aerobic surface layer relative to the underlying anaerobic layer (Reddy and Patrick, 1977). The importance of aerobic-anaerobic soil conditions for the simultaneous occurrence of nitrification-denitrification reactions resulting in nitrogen loss to the atmosphere has been discussed by several researchers (Patrick and Reddy, 1976; Smith et al., 1976; Reddy et al., 1976).

The role of denitrification in the conversion of nitrate-nitrogen to gaseous end products such as nitrogen or nitrous oxide gas has been extensively discussed (Goering and Dugdale, 1966; Keeney et al., 1971; Engler and Patrick, 1974; Chen et al., 1972; Patrick and Reddy, 1976). The influence of redox potential and pH conditions on the rate of denitrification in flooded soils has also been recently investigated (Van Cleemput and Patrick, 1974; Dawson and Murphy, 1972; Van Cleemput et al., 1976). Other factors known to influence denitrification reactions include ammonium diffusion, dissolved oxygen concentration, organism type, organism concentration, plant growth, carbon:nitrogen ratio, temperature and presence of toxic metals (Painter, 1970; Woldendorp, 1963; Reddy et al., 1976; Brezonik, 1977). However, little information is available on the relative magnitude of gaseous nitrogen losses of applied nitrogen in a soil-grass system.

Catchpoole (1975) reported that gaseous loss of applied nitrogen-15 from a Rhode grass-pasture field microplot reached as high as 27% when the soil was waterlogged. Gaseous losses of applied nitrogen were reported to be small or absent at a soil moisture content below field capacity.

Stefanson (1976) measured the denitrification losses of applied nitrate-nitrogen in reconstituted soil profiles in sealed

growth chambers. His results show that plant growth had a stimulating effect on the reduction of nitrate-nitrogen to gaseous nitrogen (nitrogen gas and nitrous oxide) in a cropped soil. In a pasture soil, on the contrary, plant growth generally had little effect on denitrification rate. This difference in nitrate reduction was attributed to the organic carbon level in the soil under study. In an earlier study on the losses of volatile nitrogen from agricultural soils in sealed growth chambers, Stefanson (1973) reported significantly higher loss of applied nitrate-nitrogen compared to ammonium-nitrogen. The major component of these losses was nitrogen gas with lesser quantities of nitrous oxide. However, both gases were shown to be produced by biological denitrification of soil nitrate. Significant gaseous nitrogen losses of applied nitrogen through nitrification-denitrification reactions in land treatment of wastewater has not been reported, although it has been hypothesized to occur in overland flow systems and is known to be significant in rice paddies and marsh areas (Tusneem and Patrick, 1971; Carlson et al., 1974; Reddy and Patrick, 1977).

The major factor in nitrogen removal in land treatment systems is plant uptake (Rickard, 1972; Hunt, 1972; Carlson et al., 1974). Removal of 42% of the nitrogen applied in cannery wastewater by reed canary grass has been reported for the Campbell Soup Company, Paris, Texas overland flow treatment system. Carlson et al. (1974) reported that 31% of nitrogen applied in a secondarily treated municipal effluent was removed by the grass sod in an overland flow test model maintained at a 2% slope. In a similar study of overland flow treatment of wastewater applied to a clay soil-reed canary grass system, 75.9% of the applied nitrogen was shown to be incorporated into grass tissue (Hoeppel et al., 1974).

Biological immobilization of added nitrogen in the organic fraction and fixation of added ammonium-nitrogen by the soil exchange complex are also important mechanisms in removing applied nitrogen and account for substantial portions of applied nitrogen (Wolk, 1973; Yoshida and Ancojas, 1973; Carlson et al., 1974; Hoeppel et al., 1974; Catchpoole, 1975).

It is evident that various mechanisms responsible for nitrogen transformations in terrestrial soils, wetlands and lakes are well described in the literature. However, quantitative data on the relative importance of various nitrogen removal processes such as plant uptake, denitrification and ammonia volatilization are lacking. Most of the overland flow experiments have been performed using unlabelled nitrogen source which may only reflect crude approximations of nitrogen removal efficiencies measured for various processes due to a much larger pool of indigenous soil nitrogen compared to wastewater nitrogen (Carlson et al., 1974; Hoeppel et al., 1974). It is therefore necessary that

labelled nitrogen should be used to compute a more reliable estimate of nitrogen removal efficiencies.

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The objectives of research studies reported in this section were:

1. To evaluate the role of nitrification-denitrification reactions, ammonia volatilization, plant uptake of applied labelled nitrogen and immobilization of inorganic nitrogen-15 in nitrogen removal in an overland flow treatment of wastewater.

2. To study the gaseous nitrogen losses of applied labelled nitrogen in sealed growth chamber from soil-plant systems.

3. To study the effects of rhizosphere and nitrogen forms on the distribution of applied labelled nitrogen in various effluent, soil and plant components.

4. To study the effects of nitrogen forms on the kinetics of nitrogen-15 loss in soil-plant systems simulating overland flow conditions.

DESCRIPTION OF SOILS USED

Bulk samples of surface soil were collected from various sites in Louisiana and Mississippi for the overland flow and laboratory studies. The soil samples were partially air dried and passed through a 0.63-cm mesh screen. The samples were thoroughly mixed and stored in 18-gallon covered plastic containers until use. Some properties of the soils used are listed in Table 3.

EXPERIMENT 1. FATE OF APPLIED AMMONIUM-NITROGEN IN AN OVERLAND FLOW TREATMENT IN MHOON SOIL-RYE GRASS SYSTEM

Experimental Procedures

In a test container described earlier, 66.4 kg of Mhoon soil was uniformly packed and 30 g of rye grass seed was mixed with the top few millimeters of soil. When the plants were seven weeks of age the test container was transferred to the room fitted with proper lights for normal plant growth. Tap water was applied for a few days to check the flow rates and overflow pattern. Platinum electrodes were installed at various depths across the length of the test model to monitor redox potential values. Four days after the installation of platinum electrodes, 6 liters of distilled deionized water was applied at the rate of 18 ml/minute, and ammonium-nitrogen and nitrate-nitrogen, were

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TABLE 3. CHARACTERISTICS OF SOILS USED IN VARIOUS EXPERIMENTS

Soils			
Parameter	Mhoon silt loam	Olivier silt loam	Grenada silty loam
Location	USDA Ben Hur Research Farm, Baton Rouge, Louisiana	Burden Research Plantation, Baton Rouge, Louisiana	Waterways Experiment Station, Corps of Engineers, Wastewater treatment site, Utica, Mississippi
Subgroup	Typic Fluvaquents	Aquic Fragiudalfs	Typic Albaqualfs
Clay, %	13.1	8.3	23.0
Silt, %	42.9	88.7	74.0
Sand, %	44.0	3.0	3.0
pH	5.8	6.7	6.4
Cation exchange capacity meq/100 g	11.0	6.2	9.2
Organic carbon, %	1.0	0.8	0.9

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determined in the runoff and subflow collected. Then 6 liters of water, equivalent to 1.5 cm/day containing 50 micrograms (μg) ammonium-nitrogen/ml as ammonium sulfate (5.3 atom % labelled nitrogen) were applied at a flow rate of ≈ 18 ml/minute. The concentration of ammonium- and nitrate-nitrogen were determined in the surface runoff and subflow. A total of 18 influent applications were made during the length of experiment. After the influent application was stopped, rye grass plants were harvested separately from 0- to 37-cm, 37- to 74-cm, 74- to 111-cm, and 111- to 148-cm regions downslope and analyzed for total nitrogen. Soil samples were collected from 0- to 2.5-cm, 2.5- to 5.5-cm, and 5.5- to 11-cm depths across the length of the test container and analyzed for ammonium-, nitrate-, and organic-nitrogen. The concentration of labelled nitrogen in the various effluent, soil and plant components were determined by mass spectrometry. The pH of soil samples collected was determined in the 1:1 soil-water ratio using a glass-combination electrode.

Results and Discussion

Redox Potential Measurements--

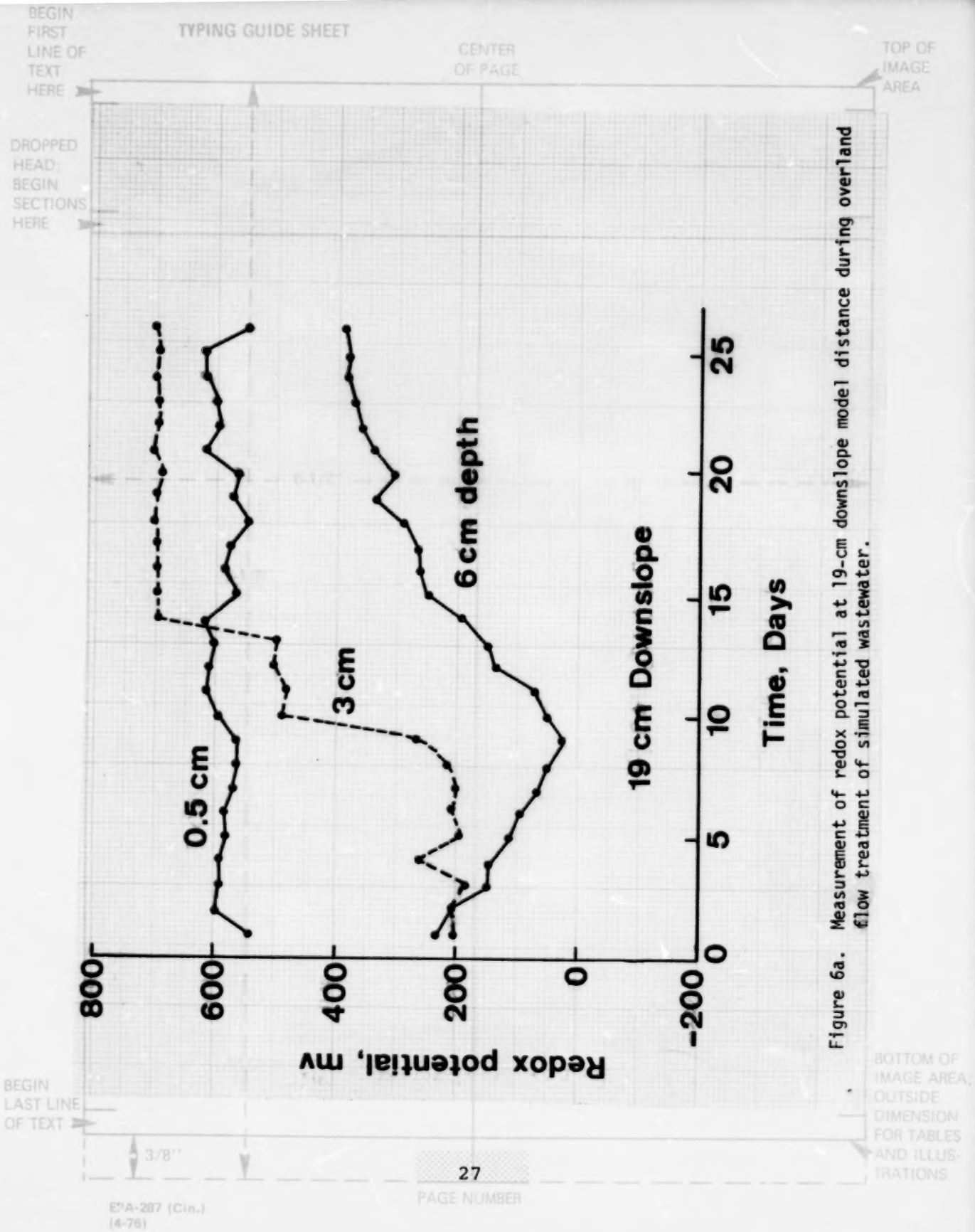
Data presented in Figures 6a and 6b and Table B-1 indicate that the top 0.5-cm soil layer of the soil-rye grass test model remained well oxidized during the length of the experiment. Below this soil depth, redox potential values ranged from well oxidized to very reduced (see values for 3- and 6-cm depths, Figures 6a and 6b, and Table B-1). These aerobic-anaerobic zones in the soil mass are known to facilitate nitrification-denitrification processes and enhance nitrogen losses to the atmosphere (Tusneem and Patrick, 1971; Broadbent and Tusneem, 1971; Yoshida and Padre, 1974; Patrick and Reddy, 1976; Reddy et al., 1976).

Soil pH Measurements--

The pH of soil samples collected after rye grass harvest was measured in a 1:1 soil-water ratio after allowing the suspension to equilibrate for 30 minutes. The data given in Table 4 show that the pH of the surface 2.5-cm layer was considerably lower (5.1 to 5.3) than the 2.5- to 11-cm soil layers (5.7 to 6.0). This low soil pH may be inhibiting both nitrification and denitrification reactions in the study, as the growth of nitrifiers and denitrifiers is reduced at pH values below neutrality (Dawson and Murphy, 1972; EPA, 1975; DeLeval and Remacle, 1976). This suggests the need of liming the soil for optimum microbial growth in future experiments.

Recovery of Added Labelled Ammonium-Nitrogen in Various Components--

Data summarized in Table 5 indicate that most of the added labelled nitrogen recovered in the effluent was in the ammonium form. Essentially all of this labelled ammonium-nitrogen



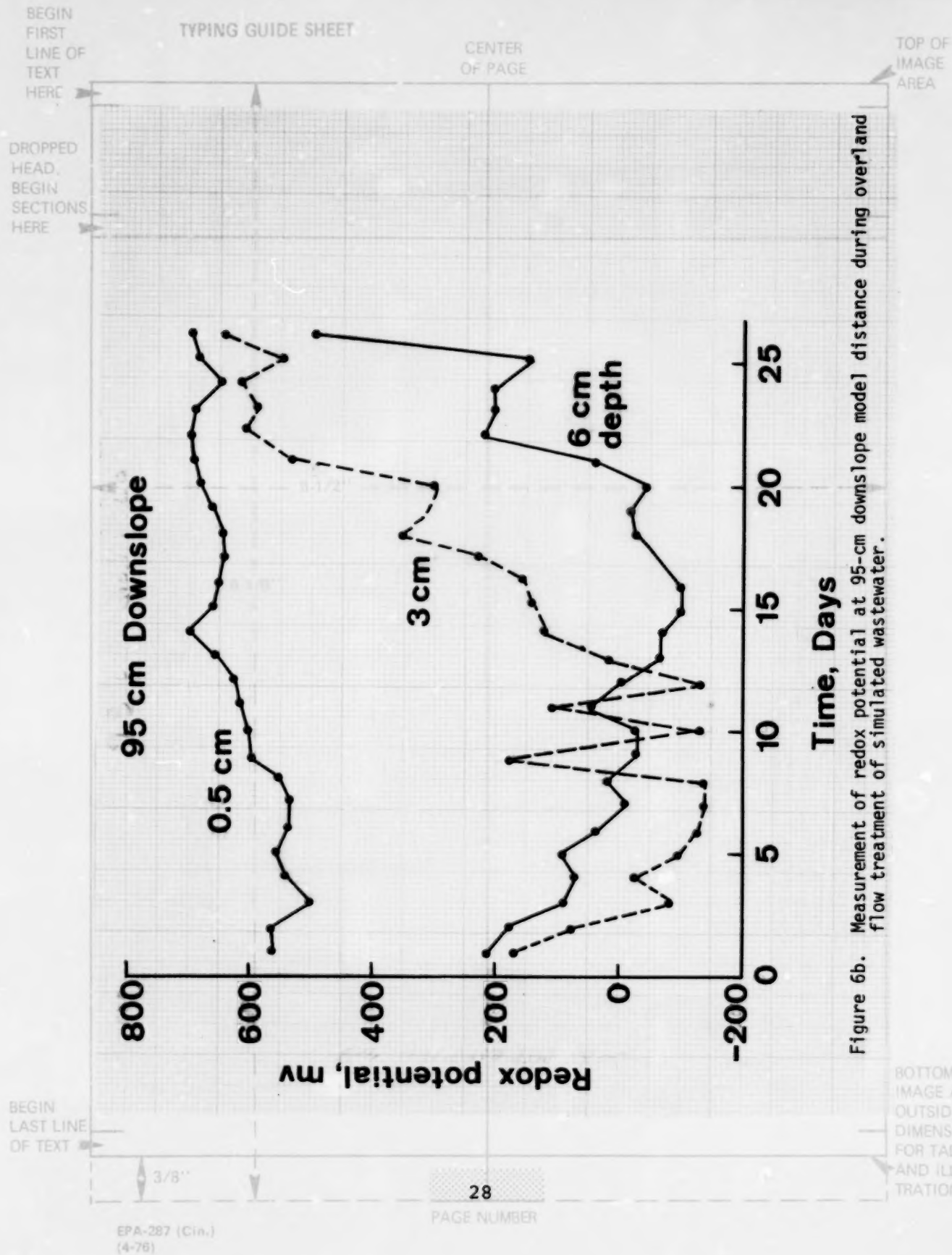


TABLE 4. EFFECT OF SOIL DEPTH AND MODEL DISTANCE ON 1:1 SOIL pH DETERMINED AFTER RYE GRASS HARVEST (MHOON SOIL, EXPERIMENT 1)

Distance downslope cm	Soil depth, cm		
	0-2.5	2.5-5.5	5.5-11.0
0-37	5.23	5.90	5.88
37-74	5.20	5.80	5.90
74-111	5.30	6.03	5.93
111-148	5.15	5.75	5.80

TABLE 5. RECOVERY OF ADDED LABELLED AMMONIUM-NITROGEN IN RUNOFF AND SUBFLOW (EXPERIMENT 1)

Ammonium-nitrogen applied		Ammonium-nitrogen recovered		Nitrate-nitrogen	
		Runoff	Subflow	Runoff	Subflow
		mg N			
Total	5100	1513.60	70.69	27.82	13.69
%	100	29.68	1.39	0.54	0.27

recovered was present in the runoff. Less than 1% of total labelled nitrogen was present in the nitrate form in both runoff and subflow whereas 30% of added nitrogen-15 was in the ammonium form. This low recovery of added ammonium-nitrogen in the nitrate form indicates that the process of nitrification (biological oxidation of ammonium-nitrogen to nitrate-nitrogen) in the flowing water during the overland flow treatment was essentially nonexistent.

Approximately 68% of added labelled nitrogen not found in the runoff and subflow may have been adsorbed by the soil, incorporated into the organic fraction, taken up by the plants, or lost to the atmosphere through denitrification reactions. Analyses of soil samples collected after rye grass harvest show that a substantial amount of added nitrogen was present in the

top 2.5-cm soil layer in the ammonium as well as nitrate form (Table B-2). The concentration of ammonium-nitrogen in the top 2.5-cm soil layer was slightly higher than that of nitrate-nitrogen. However, in the 2.5- to 11-cm soil layers, nitrate-nitrogen concentration was two to five orders of magnitude greater than ammonium-nitrogen. The difference in the organic nitrogen fraction due to added ammonium-nitrogen was not visible in the quantitative analyses.

To determine more precisely the distribution of added ammonium-nitrogen in various soil fractions, nitrogen-15 was analyzed, and the proportion of nitrogen contributed by the added ammonium-nitrogen was calculated. The data shown in Table 6 indicate 8.55% of total ammonium-nitrogen added through overland flow treatments was adsorbed by the soil complex in the ammonium-nitrogen form at the end of the experiment.

Approximately 6% of labelled nitrogen was recovered in the nitrate form in the soil samples analyzed after rye grass harvest. This strongly indicates that some biological oxidation of added ammonium-nitrogen was occurring in the soil and especially in the top 2.5-cm surface layer, as most of the nitrate-nitrogen was present in this layer.

A substantial amount of applied labelled ammonium-nitrogen was taken up by the rye grass plants growing during the overland flow treatment. The recovery of added labelled nitrogen in the plants accounted for approximately 41% of the total applied nitrogen (Table 6).

A balance sheet calculated for the added labelled nitrogen shows that 98.1% of the total was recovered in the effluent water, soil, and plants (Table 7). Thus, only 2.91% of labelled nitrogen was unaccounted for, which may be assumed as lost to the atmosphere through denitrification reactions or ammonia volatilization. The extent of this applied ammonium-nitrogen-15 loss was determined under sealed growth chamber conditions in the following experiment.

EXPERIMENT 2. A STUDY OF GASEOUS NITROGEN LOSS OF ADDED LABELLED AMMONIUM-NITROGEN IN AN OVERLAND FLOW TREATMENT IN MHOON SOIL-BERMUDA GRASS SYSTEM IN SEALED GROWTH CHAMBER

Experimental Procedures

In a test container described earlier (Figure 1), 70.9 kg of air dried soil was uniformly packed and planted to bermuda grass (*Cynodon dactylon*, L.) collected from a field on the Louisiana State University campus. The sod was allowed to dry for a day and excess soil was shaken off the root mass before placing on

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TABLE 6. RECOVERY OF ADDED LABELLED AMMONIUM-NITROGEN IN SOIL AND PLANT COMPONENTS IN MHOON SOIL- RYE GRASS TEST MODEL (EXPERIMENT 1)

	Ammonium nitrogen applied	Soil nitrogen			Plant nitrogen
		ammonium	nitrate	organic	
		mg ¹⁵ N			
Total *	5100	435.89	318.47	494.42	2076.70
%	100	8.55	6.24	9.67	40.72

* Labelled ammonium-nitrogen applied in 17 overland flow treatments.

TABLE 7. DISTRIBUTION OF ADDED LABELLED AMMONIUM-NITROGEN IN THE SOIL-WATER PLANT SYSTEM DURING THE OVERLAND FLOW TREATMENT IN MHOON SOIL - RYE GRASS TEST MODEL (EXPERIMENT 1)

System	¹⁵ N Recovered	
component	mg N	%
Water effluent	1625.80	31.88
Soil	1248.78	24.48
Plant	2076.70	40.72
¹⁵ N unaccounted for	148.72	2.92

* 5100 milligrams labelled ammonium-nitrogen applied in 17 treatments.

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top of the soil surface. Sod and soil were compressed evenly and sprinkled with tap water. Bermuda grass was grown for several months and trimmed to about 15-cm height for a few times to establish a good bermuda grass cover. The test container and whole soil-plant assembly was sealed air-tight in a 0.63-cm thick plexiglas box with silicon rubber and epoxy glue. The objective of this closed system was to monitor the evolution of gaseous nitrogen as a result of sequential nitrification-denitrification processes occurring in the soil-plant system following an overland flow treatment with labelled ammonium-nitrogen. Two sampling ports for gas sampling, a thermometer to monitor temperature of the inner atmosphere, and an outlet fitted with a serum cap for purging were installed. Provisions were made to add influent to the system as well as for effluent outflow (runoff and subflow) without any external gases entering the closed system. The temperature in the closed system was maintained at $31^{\circ}\text{C} \pm 1^{\circ}\text{C}$ by constantly circulating cool water in the system through copper tubing running inside the closed system. A schematic diagram of the overland flow treatment model in a sealed growth chamber is given in Figure 7. After this the soil-plant closed system was purged with a 4:1 mixture of argon and oxygen gases for 24 hours to bring the level of nitrogen gas in the system to a minimum. Six liters of water containing 100 μg ammonium-nitrogen-15/ml (containing 10.5 atom % nitrogen-15) were applied to the sealed system at a flow rate of 16.8 ml/minute on alternate days, and runoff and subflow were collected together. Gas samples were collected from the closed atmosphere and analyzed for labelled nitrogen gas using Dupont Model 21-614 mass spectrometer according to the procedure described by Reddy (1976). The experiment was run for 30 days and the proportions of added ammonium-nitrogen recovered in the effluent and that in the gaseous atmosphere were calculated.

Results and Discussion

The results summarized in Table 8 show that 27% of added ammonium-nitrogen was recovered in the ammonium form in the combined runoff plus subflow water. Nitrate-nitrogen determined in the combined runoff plus subflow was less than 0.3%. This indicates that during the six-hour contact period between ammonium solution and the soil surface, oxidation of ammonium to nitrate was practically nonexistent. Similar results were obtained earlier in Experiment 1 where rye grass was grown instead of Bermuda grass.

Approximately 73% of applied nitrogen not recovered in the combined runoff plus subflow may have been taken up by the plants, retained by the soil, or escaped into the atmosphere above the soil surface as nitrogen gas, nitrous oxide, or as ammonia. To measure the extent of gaseous nitrogen production, gas samples were analyzed for labelled nitrogen by mass spectrometry during the length of the experiment. The production of

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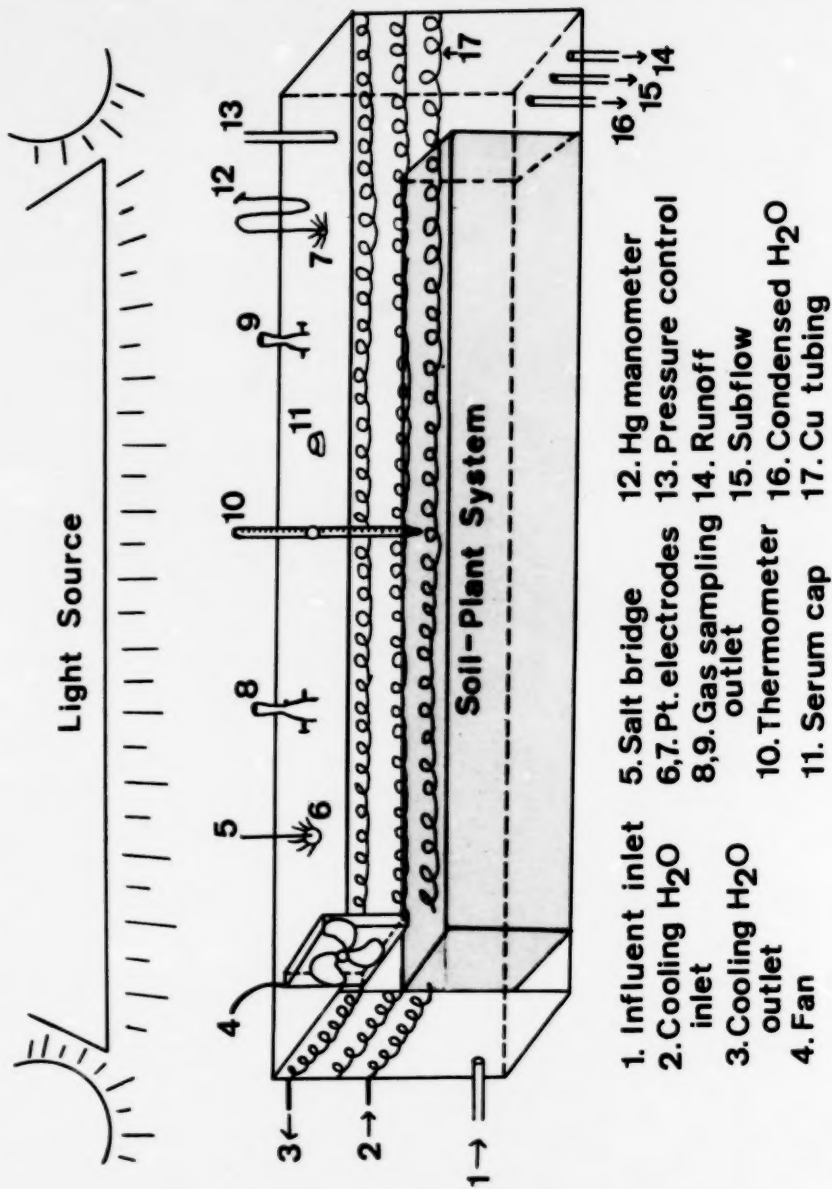


Figure 7. A schematic diagram of the sealed overland flow treatment model used in the nitrogen transformations' study.

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nitrous oxide was not measured in this study. Data plotted in Figure 8 show that the concentration of labelled nitrogen gas produced increased three-fold towards the end of the experiment. This increase in nitrogen gas concentration indicates that the processes of nitrification-denitrification were taking place in the overland flow treatment in the system. However, the amount of labelled nitrogen gas detected under the conditions of the experiment was relatively small (approximately 3% of added nitrogen; Table 8).

TABLE 8. BALANCE SHEET OF LABELLED AMMONIUM-NITROGEN APPLIED TO A SEALED MHOON SOIL-BERMUDA GRASS OVERLAND FLOW SYSTEM ESTABLISHED AT 2% SLOPE (EXPERIMENT 2)

System component		¹⁵ N recovered
Total ammonium-nitrogen applied	=	9.494 g
Average ammonium-nitrogen application	=	0.633 g day ⁻¹
Total ammonium-nitrogen recovered in the combined runoff plus subflow water	=	2.577 g
% of total ammonium-nitrogen applied	=	27.14%
Total nitrate-nitrogen recovered in the combined runoff plus subflow water	=	0.025 g
% of total ammonium-nitrogen applied	=	0.27%
Total ammonium-nitrogen not recovered in the combined runoff plus subflow water	=	6.892 g
% of total ammonium-nitrogen not recovered	=	72.59%
Gaseous nitrogen loss as determined by labelled nitrogen gas	=	3.34%
Length of experiment	=	30 days

The results obtained in Experiment 1 where rye grass was grown were also similar in such that about 3% of the added labelled nitrogen not accounted for was thought to be lost through denitrification.

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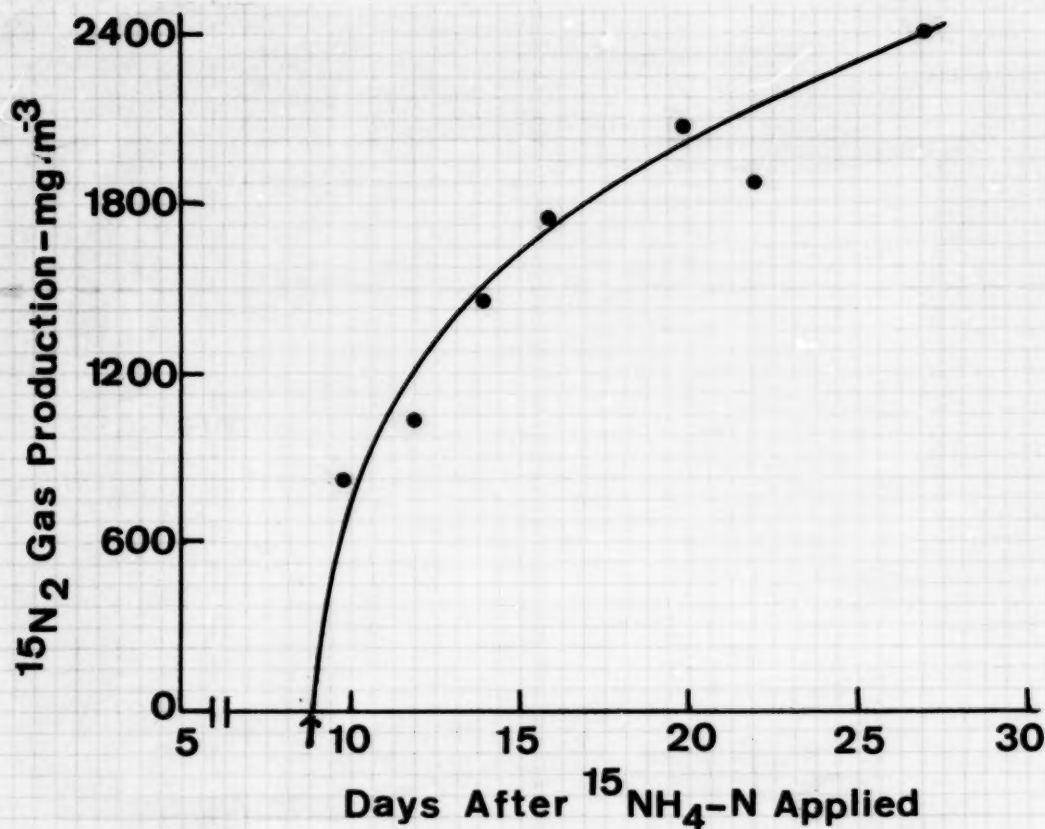


Figure 8. Gaseous nitrogen-15 production of applied ammonium-nitrogen in a sealed overland flow system established on Mhoon soil put on 2% slope with Bermuda grass growing. The arrow shows that on the 9th day after nitrogen was applied the enclosed system was purged with 4:1 mixture of argon and oxygen gases.

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In this experiment Bermuda grass plants or soil samples collected for the plant harvest were not analyzed for nitrogen components. The pH of soil samples determined after plant harvest was 5.9 across the length of the test model.

The results of Experiments 1 and 2 indicated that although the process of nitrification-denitrification was taking place in the overland flow system, the magnitude of nitrogen loss was insignificant. The plant and soil demand for the added nitrogen probably resulted in a major part of the added labelled nitrogen being combined in the soil and plant system. The relatively small fraction of added nitrogen (8.55% labelled ammonium, 6.24% labelled nitrate in the soil, Table 6) remaining in the soil at the end of Experiment 1 which is a potential source of biological nitrification-denitrification reactions may also explain low gaseous nitrogen loss. Nitrification-denitrification processes may also be limited in the system due to following factors: 1) unfavorable low soil pH in Experiments 1 and 2 may have adversely affected the oxidation of added ammonium-nitrogen resulting in less nitrate-nitrogen available for denitrification; 2) low soil pH affects the growth of denitrifiers resulting in reduced gaseous nitrogen losses; 3) since no readily available energy source was added in the experiments, this may be a limiting factor in the reduction of nitrate. Organic carbon furnishes energy for the growth of denitrifying bacteria and also serves as a hydrogen donor for the reduction of nitrate to nitrous oxide or nitrogen gas. Published literature have shown that the addition of readily oxidizable carbon source such as glucose, sucrose, or mannitol resulted in rapid denitrification (Bremner and Shah, 1958; McGarity, 1961); and 4) the short duration of the overland flow experiments may be a factor in lower gaseous nitrogen losses determined in the experiments.

EXPERIMENT 3: THE DISTRIBUTION OF APPLIED LABELLED AMMONIUM-NITROGEN IN VARIOUS COMPONENTS OF OVERLAND FLOW TREATMENT MODEL IN OLIVIER SOIL-BERMUDA GRASS SYSTEM IN A SEALED GROWTH CHAMBER

The results of mass balance of applied ammonium-nitrogen in an overland flow treatment model discussed in Experiments 1 and 2 in this section had indicated an insignificant gaseous nitrogen loss from the system. Acidic soil pH and an insufficient supply of easily available energy source were thought to be partially responsible for the inhibition of nitrification-denitrification reactions in the soil-plant system resulting in a reduced gaseous nitrogen production. This study was designed to create favorable conditions for the occurrence of nitrification-denitrification reactions in an overland treatment model and thus to improve the nitrogen removal efficiency of the soil-plant system.

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Experimental Procedure

The test container for the overland flow model was constructed of a 1.27-cm thickness of plywood with inside dimensions of 30-cm width, 152-cm length and 13-cm depth and has been described in Section 3 (Figure 1). Olivier silt loam soil collected from Burden Experiment Farm, Baton Rouge, Louisiana, characterized in Table 3, was limed with calcium carbonate to pH 6.5 and was used in this experiment.

In the test container described above, 68 kg of Olivier soil, calculated on oven dry weight basis, was uniformly packed to a 12.5-cm depth and planted to Bermuda grass sod. Bermuda grass was grown for several months to establish a good grass cover. An additional application of calcium carbonate, equivalent to 10 milliequivalents/100 g of soil was made on the soil surface three weeks prior to enclosing the soil-plant system. The experimental model was placed on a 2% slope in a room fitted with fluorescent and incandescent lights for normal plant growth. Platinum electrodes were installed in triplicate, at 1-cm and 7-cm soil depths, at two points across the length of the test container (20 cm and 120 cm downslope) to monitor redox potentials. Two weeks after the installation of the platinum electrodes the test container with the soil-plant system was enclosed in a 0.63-cm thick Plexiglas box and sealed airtight with silicon rubber. Two sampling ports for gas analysis, a mercury manometer for monitoring the pressure of the chamber's atmosphere, a thermometer, and outlets for platinum electrode wires were installed. Provisions were made for influent addition, effluent outflow and condensed water collection. The temperature of the closed system was maintained at $30 \pm 1^\circ\text{C}$ by constantly circulating a cold water-ethanol mixture (-10°C) through copper tubing running inside the closed system. A schematic diagram of the overland flow treatment model and the enclosed system is shown in Figure 7.

The sealed soil-plant system was purged with a 4:1 mixture of argon and oxygen gases for 24 hours to bring the level of nitrogen gas in the system to less than 1%. Twelve liters of solution containing 23 μg ammonium-nitrogen-15/ml (10.372 atom % nitrogen-15) and 27 μg soluble carbon/ml was applied to the closed overland flow system at a flow rate of 11.1 ml/minute. The runoff and subflow collected were recirculated for four to five days to create reduced soil conditions. No solution was then applied for one to two days and the soil-plant system was allowed to reoxidize to facilitate nitrification. Seventeen influent applications containing labelled ammonium-nitrogen and soluble carbon were made during the 90-day experiment period. Runoff and subflow collected at the end of each application were combined and analyzed for ammonium- and nitrate-nitrogen-15. Gas samples were collected from the closed system at regular intervals and analyzed for labelled nitrogen and nitrous oxide gases

using a Dupont Model 21-614 mass spectrometer. The condensed water collected from the closed system was analyzed for ammonium-nitrogen to determine the occurrence of ammonia volatilization during overflow. Redox potential measurements were made everyday to monitor the occurrence of oxidized and reduced conditions conducive to nitrification-denitrification reactions. At the end of overflow treatments plant samples were analyzed for labelled nitrogen. Soil mass was sectioned with depth and downslope length and analyzed for ammonium-, nitrate- and organic-nitrogen-15. The proportion of applied labelled ammonium-nitrogen recovered in various components was calculated as was nitrogen mass balance. The pH of the sectioned soil samples was also determined.

Results and Discussion

Redox Potential Measurements During Overland Flow Treatment--

The redox potentials were measured at 1-cm and 7-cm depths to determine the oxidation-reduction status of the surface and subsurface soil layers. The redox potential values of a surface layer of the soil-plant system ranged from +450 millivolts (mv) to +700 mv and remained well oxidized during the 90-day overland flow treatment. The redox potential values determined at the 7-cm depth fluctuated from +150 mv to +710 mv during the first 60 days of the experiment and from -180 mv to +690 mv during the latter part of the experiment (Figure 9). It is evident from the data that well oxidized conditions near the soil surface provided a favorable environment for the nitrification of added ammonium-nitrogen* retained by the soil mass. The redox potential values of the subsurface layer oscillated from reduced to oxidized to reduced conditions during the course of overflow treatments which indicate that conditions for the denitrification of nitrate-nitrogen that may have diffused down from the surface layer were occurring in the test model. Redox potential values of approximately 350 mv or less would cause the nitrate-nitrogen to be unstable and subject to denitrification reactions (Reddy and Patrick, 1975). The aerobic-anaerobic zones identified in the soil-plant system would facilitate simultaneous nitrification-denitrification processes and enhance nitrogen losses to the atmosphere (Reddy, 1976; Broadbent and Tusneem, 1971).

Mass Balance of Influent Ammonium-Nitrogen Applied to Olivier Soil-Bermuda Grass Sealed Overland Flow Model--

The runoff and subflow collected after influent applications were analyzed for ammonium- and nitrate-nitrogen to determine the proportion of added ammonium-nitrogen not retained by the soil-plant system. At the end of the 90-day overland flow treatments, the plant root and shoot mass was analyzed for nitrogen taken up by the plant. The soil mass was sectioned with depth and length

* The nitrogen data presented in this experiment is of nitrogen-15 and hence the word 'labelled' will be omitted from the text.

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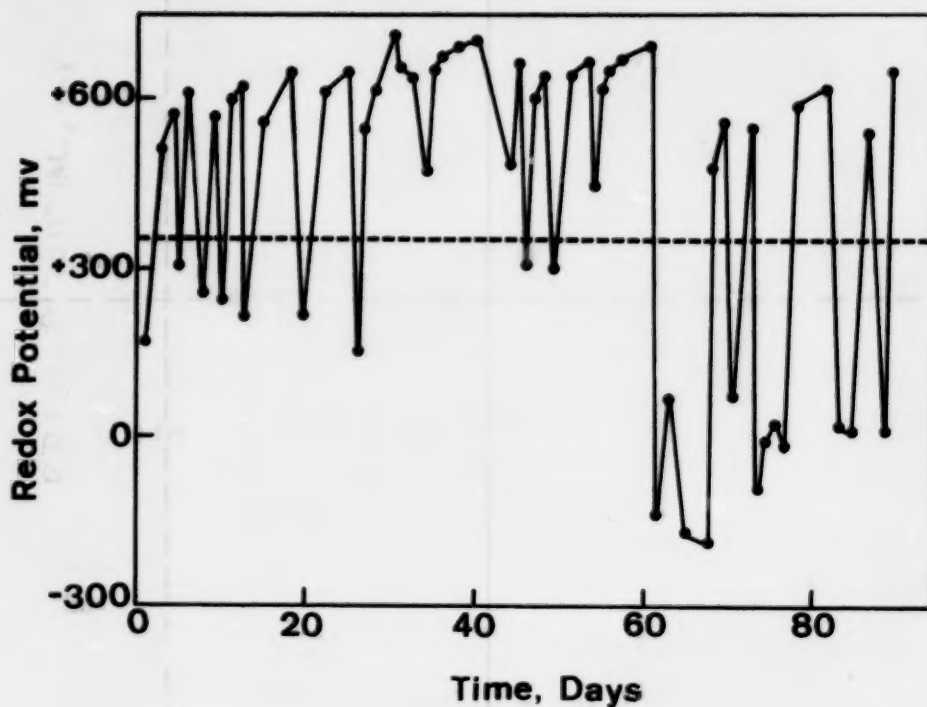


Figure 9. Redox potential values at the 7-cm soil depth for the platinum electrodes fixed at 20-cm downslope model distance during overland flow treatment of simulated wastewater.

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and analyzed for ammonium-, nitrate- and organic-nitrogen fractions. A mass balance of added ammonium-nitrogen recovered in various system components is presented in Table 9. The data indicate only 7% of added ammonium-nitrogen was determined in the effluent runoff and subflow. Most of the added nitrogen-15 recovered in the effluent was present in the ammonium form. The fraction of applied nitrogen-15 present in nitrate form in the runoff and subflow was insignificant (0.25%).

Approximately 93% of added nitrogen not found in the effluent water may have been taken up by the plants, been adsorbed by the soil complex, incorporated into the organic fraction, or lost to the atmosphere through denitrification or ammonia volatilization reactions.

The uptake of nitrogen-15 by Bermuda grass plants accounted for 23% of added ammonium-nitrogen. The aboveground plant shoots and primary roots accounted for 16.49% and 6.44% of total nitrogen-15 added, respectively. The proportion of added nitrogen-15 retained by the soil fraction amounted to 12.33% in the ammonium form, 0.32% in the nitrate form and 21.92% in the organic form. Similar to the effluent data, very little acid ammonium-nitrogen was accumulated in the nitrate form in the soil at the end of the experiment. This indicates that nitrate-nitrogen was not stable in the system and may have transformed immediately to other forms which will be discussed later in the report.

A balance sheet calculated for the added nitrogen-15 shows that 64.57% was recovered in the effluent water, plant and soil fractions (Table 9). This means that 35.43% of added nitrogen-15, a significant fraction, was unaccounted for. This nitrogen-15 may have been lost to the atmosphere through denitrification reactions or ammonia volatilization. The sealed soil-plant system was set up to monitor the evolution of nitrogen and nitrous oxide gases due to denitrification reactions occurring in the system. The data plotted in Figure 10 indicate that nitrogen gas production steadily increased with time, although not at the same rate, and a maximum concentration of over 1200 milligrams (mg) nitrogen/cubic meter was detected at the end of the 90-day overflow treatments. The proportionately greater nitrogen gas production in the last 20 days may be attributed to more reduced soil conditions in the subsurface (Figure 9) favorable to the biological denitrification of nitrate-nitrogen present in the soil. No nitrous oxide gas was detected in the closed atmosphere. The absence of nitrous oxide in the system may be due to the high soil pH, 6.6 to 7.6, which favors nitrogen gas formation (Table 10). Studies on denitrification products show that acid conditions are more favorable for the formation of nitrous oxide and nitric oxide than neutral and alkaline conditions which enhance nitrogen gas (Cady and Bartholomew, 1960; Van Cleemput et al., 1976). Also, due to high

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TABLE 9. MASS BALANCE OF AMMONIUM-NITROGEN (4742.3 mg N) ADDED TO OLIVIER SOIL-BERMUDA GRASS SEALED OVERLAND FLOW SYSTEM (EXPERIMENT 3)

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System component	15 recovered	
	mg N	% of added N
Effluent (runoff & subflow)		
$\text{NH}_4^+\text{-N}$	321.10	6.77
$\text{NO}_3^-\text{-N}$	11.87	0.25
Plant uptake		
Shoots	782.10	16.49
Roots	305.60	6.44
Soil fraction		
$\text{NH}_4^+\text{-N}$	584.79	12.33
$\text{NO}_3^-\text{-N}$	15.11	0.32
Organic-N	1039.65	21.92
Total N recovered	3060.23	64.57
N loss	1682.07	35.43
(N_2 gas)	Incomplete recovery	(2.80)
(NH_3 volatilization)	Incomplete recovery	(4.30)

solubility of nitrous oxide, traces of this gas produced in the closed system may have dissolved in the condensing water and escaped the system. The recovery of nitrogen gas in the enclosed atmosphere was not quantitative since a steady increase in the peak heights at mass/electron number of 28 and 40 in the mass spectrometric analysis (which represent nitrogen and argon gases, respectively) was detected. This indicates that the enclosed atmosphere was slowly contaminated by the outer atmosphere, possibly through the influent water application and may

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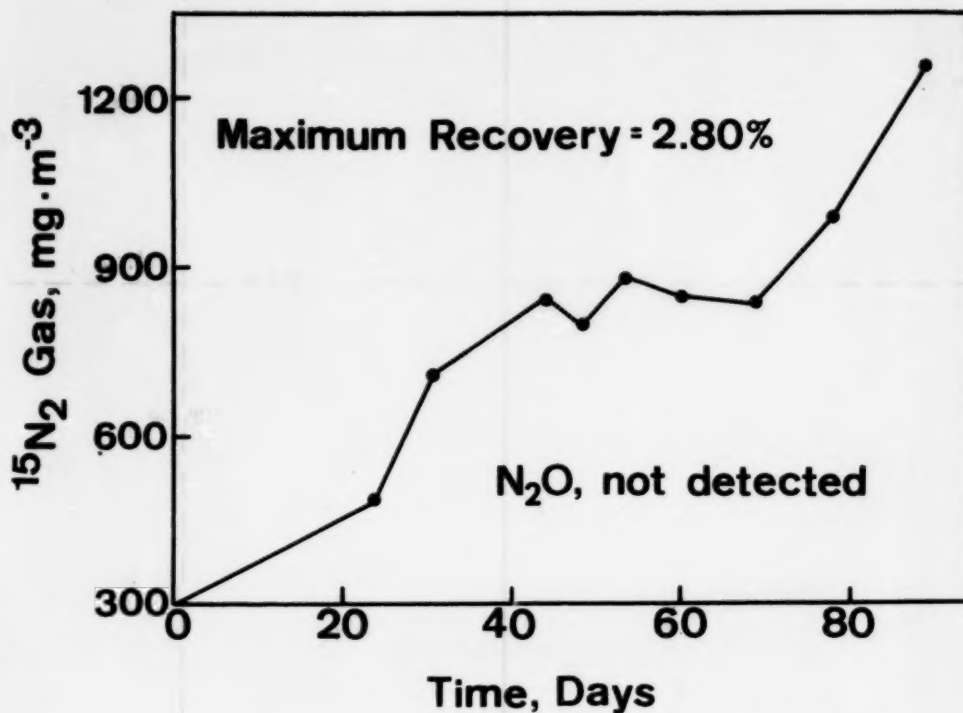
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Figure 10. Gaseous nitrogen-15 production as a function of time in a sealed overland flow Olivier soil-Bermuda grass system.

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TABLE 10. SOIL pH DETERMINED AT THE END OF OVERLAND FLOW
EXPERIMENT (OLIVIER SOIL, EXPERIMENT 3)

Soil depth cm	Distance downslope, cm			
	0-37	37-74	74-111	111-148
0-2.5	7.2	7.4	7.6	7.6
2.5-5.5	6.6	6.9	7.1	7.1
5.5-12.5	6.6	6.7	6.8	6.8

have displaced nitrogen-15 gas through runoff, subflow or condensing water outlets. In spite of the incomplete recovery of nitrogen gas, the data plotted in Figure 9 indicate the occurrence of denitrification reactions in the overflow system at the low redox potential levels.

The loss of applied ammonium-nitrogen through ammonia volatilization was detected by collecting the condensed water from the closed system in 0.1 N sulfuric acid and analyzing for ammonium-nitrogen. The recovery of this ammonia volatilized, although qualitative and incomplete, accounted for 4.3% of total nitrogen-15 added and confirmed the occurrence of ammonia volatilization process in the overflow system. Surface soil pH that ranged from 7.2 to 7.6 (Table 10) provided favorable conditions for the volatilization of applied ammonium-nitrogen. Appreciable losses of applied ammonium-nitrogen under alkaline soil conditions have been detected under laboratory and field conditions (Mills et al., 1974; Ryan and Keeney, 1975) and may be a significant process in nitrogen removal from the wastewater.

Based on the qualitative detection of ammonia volatilization and denitrification products it can be concluded that 35.43% of applied nitrogen-15 not accounted for in the mass balance sheet was lost to the atmosphere through biological denitrification and ammonia volatilization reactions.

Distribution of Soil Nitrogen-15 Fraction as a Function of Soil Depth and Downslope Length--

The efficiency of nitrogen removal by the soil mass investigated by determining the concentration gradients of various nitrogen forms at the end of the experiment. The soil was divided into 0- to 37-cm, 37- to 74-cm, 74- to 111-cm and 111- to 148-cm sections downslope from the point of influent application. Each section was then sliced to 0- to 2.5-cm, 2.5- to 5.5-cm and 5.5- to 12.5-cm depths and analyzed for soluble and exchange

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ammonium-nitrogen, soluble nitrate-nitrogen and organic-nitrogen-15. The data summarized in Table 11 indicate that ammonium-nitrogen decreased sharply with slope and this trend was obvious

TABLE 11. DISTRIBUTION OF INFLUENT AMMONIUM-NITROGEN IN VARIOUS SOIL FRACTIONS DETERMINED AT THE END OF OVERFLOW TREATMENTS IN SEALED SOIL-PLANT SYSTEM (EXPERIMENT 3)

Soil depth cm	Distance downslope, cm			
	0-37	37-74	74-111	111-148
		<u>$^{15}\text{NH}_4^+\text{-N}$, $\mu\text{g/g}$ soil</u>		
0.2.5	33.18	14.38	4.08	1.12
2.5-5.5	28.74	12.44	1.82	0.81
5.5-12.5	14.73	4.27	2.48	1.48
		<u>$^{15}\text{NO}_3^-\text{-N}$, $\mu\text{g/g}$ soil</u>		
0-2.5	0.32	0.36	0.37	0.17
2.5-5.5	0.21	0.26	0.24	0.17
5.5-12.5	0.20	0.24	0.21	0.16
		<u>Organic ^{15}N, $\mu\text{g/g}$ soil</u>		
0-2.5	87.44	48.34	18.21	3.90
2.5-5.5	31.12	10.94	3.57	1.31
5.5-12.5	12.22	6.88	5.90	3.05

at all soil depths studied. A consistent decrease in ammonium-nitrogen concentration with depth was also observed in the 0- to 37-cm and 37- to 74-cm sections. No accumulation of nitrate-nitrogen occurred at the end of the experiment and the concentration of residual nitrate-nitrogen was insignificant (0.16 to 0.37 μg nitrate-nitrogen-15/g soil, Table 11). The concentration gradient of organic nitrogen-15 with depth and with distance downslope was similar to that of ammonium-nitrogen.

The accumulation of ammonium- and organic-nitrogen in the upper one-half of the test model suggests that the capacity of the soil complex to adsorb ammonium-nitrogen was not saturated at any point. Once retained by the soil complex, the ammonium-nitrogen may have been immobilized by the organic carbon applied with the influent, utilized by the soil microbes present in the soil or taken up by the plants. Since the surface soil was normally oxidized, it facilitated nitrification reaction resulting in nitrate nitrogen which diffused downward and underwent biological denitrification and lost to the atmosphere. This sequential immobilization and nitrification-denitrification processes most probably resulted in adsorption sites constantly being available for ammonium adsorption and the applied ammonium-15 did not move appreciably beyond one-half of the test model length. Similar results were reported by Hoepfel et al. (1974) for the removal of cannery wastewater nitrogen in a 3-m long overland flow model. They found that about 50% of the ammonium- and nitrate-nitrogen losses from the amended wastewater were incurred within the initial 30 cm. Law et al. (1969) also suggested a nonlinear pattern in nitrogen removal rate with slope in a grassland with cannery wastewater spray irrigation. They reported 15.0, 0.70, and 1.0 parts per million (ppm) total nitrogen after 0, 12.19, and 30.48 m of overland flow, respectively. The relative distribution of these nitrogen forms may be different in the long-term overflow models where the system may reach an equilibrium stage resulting in the mineralization of organic-nitrogen. Plant removal, ammonia volatilization, denitrification processes, nitrate leaching, and runoff will be the limiting factors in the removal of wastewater nitrogen under such conditions.

EXPERIMENT 4. EFFECT OF AMMONIUM-NITROGEN LEVELS ON GASEOUS NITROGEN LOSS IN MHOON SOIL-RICE SYSTEM IN A SEALED GROWTH CHAMBER

This experiment was designed to study the distribution of increasing concentrations of applied labelled ammonium-nitrogen in the gaseous, soil and plant components in a sealed atmosphere. The enclosed assembly was designed to eliminate any unaccounted for losses of applied nitrogen that may have occurred in the sealed overhead flow treatment model described in Experiment 3 and hence to prepare a more accurate mass balance of added labelled nitrogen. Simulated overland flow treatment was achieved through repeated aerobic-anaerobic cycles to allow nitrification-denitrification reactions to occur. The production of nitrogen and nitrous oxide gases and ammonia volatilized was monitored to account for the losses of applied ammonium-nitrogen through these processes.

Experimental Procedures

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Mhoon silt loam soil, limed with 60 millequivalents CaCO_3 /100 g soil to raise the pH to 7.0 was used for this study. Limed soil, equivalent to 1506 g of oven dry weight was transferred to 0.63 cm thick walled Plexiglas cylindrical containers measuring 14-cm in diameter and 12.5-cm in length and sealed at one side. The soil depth in the test containers was 8-cm. Soil in test containers was equilibrated at 35% moisture for three weeks to allow calcium carbonate to react with the soil. Rice (*Oryza sativa* L.) seedlings (variety saturn) were grown for three weeks before treatment applications were made. A pretreatment application of 200 μg unlabelled ammonium-nitrogen/g soil as ammonium phosphate and 500 μg carbon/g soil as dextrose was made when the seedlings were 10 days of age. Soil moisture in the soil-plant system was maintained at 35% level.

Description of Sealed Growth Chamber System--

Pyrex glass desiccators with a 9.4 liter capacity were used for the enclosed atmosphere study. The desiccator lid was fitted with high vacuum 2 millimeters (mm) glass stopcock and a ground glass T10/30 female joint for gas sampling. Special ground glass tubes fitted with high vacuum 2-mm stopcocks were used for gas sampling. Cold water was constantly circulated through a 0.63-cm copper tubing coiled inside the desiccator to maintain a constant soil-plant-atmosphere temperature of $28 \pm 1^\circ\text{C}$. A schematic diagram of the desiccator assembly is given in Figure 11.

Treatment Application and Gas Analysis--

Labelled ammonium-nitrogen (49.664 atom % ^{15}N), as ammonium sulfate, was applied at the rate of 100, 150, and 200 μg nitrogen/g soil to the Mhoon soil-rice system. An undisturbed soil core of Grenada soil established with rye grass (described later in Experiment 5) and amended with 150 μg nitrogen/g soil was also included in this study. The moisture content of the soil was adjusted to 25% and the containers transferred to the desiccator assembly. Fifty milliliters of 0.1 N sulfuric acid was placed in each desiccator to absorb any ammonia gas volatilized. A carbon dioxide trap containing 30 g of potassium hydroxide pellets was attached to the container walls to absorb excessive carbon dioxide buildup that may be injurious to plant growth. The desiccator assembly was sealed and the enclosed gaseous atmosphere was analyzed for nitrogen, oxygen, carbon dioxide and nitrous oxide using a mass spectrometer. Nitrous oxide in gas samples was analyzed by passing the sample through an ethanolamine trap to eliminate carbon dioxide gas which appears at the same mass/electron number (44) as nitrous oxide in the mass spectrum. The gaseous atmosphere was analyzed after eight days to detect any nitrogen or nitrous oxide evolved under oxidized soil conditions. The eight-day incubation of soil-plant system at $\approx 25\%$

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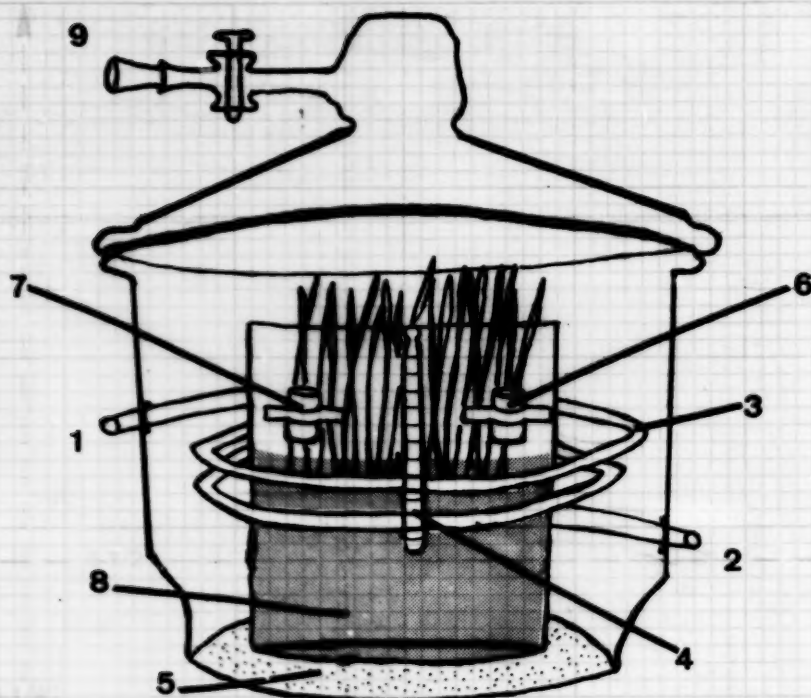
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1. Cooling H₂O inlet

2. Cooling H₂O outlet

3. Copper tubing

4. Thermometer

5. NH₃ trap

6. CO₂ trap

7. H₂S trap

8. Plexiglass container
with soil and plants

9. Gas sampling and
pressure monitor-
ing outlet

Figure 11. A schematic diagram of the sealed dessicator assembly used for the determination of gaseous nitrogen losses in a soil-plant system.

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moisture level was allowed to facilitate nitrification of added ammonium-nitrogen prior to the occurrence of denitrification reaction.

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The system was then opened, and evolved ammonia gas absorbed by the acid trap was analyzed. The moisture content of the soil was then increased to 50% and 500 μ g soluble carbon/g of soil was added to provide energy source for the denitrifiers and create reduced soil conditions. The carbon dioxide and ammonia gas traps were replaced. A trap of 1.0 N zinc acetate solution was attached to the soil-plant container walls to absorb any hydrogen sulfide produced under reduced soil conditions. The desiccator assembly was sealed, and the enclosed gaseous atmosphere was analyzed at regular intervals for nitrogen and nitrous oxide gases.

The sealed desiccator system was reopened after 11 days and ammonia gas in the sulfuric acid trap was analyzed. The soil-plant system was then maintained at about 25% for the next eight days without sealing the desiccator assembly to allow for the nitrification of remaining ammonium-nitrogen. The moisture content of the soil was then raised to 50%, traps for carbon dioxide, ammonia and hydrogen sulfide gases were replaced and the desiccator assembly was sealed. The production of nitrogen and nitrous oxide gases as a result of denitrification of nitrate-nitrogen were monitored for the next eight days.

Soil and Plant Nitrogen Analysis--

After the completion of second denitrification cycle the soil was analyzed for ammonium-, nitrate-, and organic-nitrogen. The plant samples were analyzed for total nitrogen. The proportion of labelled nitrogen in various gaseous, soil, and plant fractions contributed from the added labelled ammonium-nitrogen was calculated and a mass balance was prepared.

Results and Discussion

Measurements of Denitrification Products During Oxidation-Reduction Cycles in Mhoon-Soil Rye Grass Sealed System--

The soil-plant system was maintained under aerobic soil conditions for eight days after the addition of labelled ammonium-nitrogen. No nitrogen or nitrous oxide gases were detected during this period indicating the process of denitrification was not occurring when soil-plant system was maintained at 25% moisture. It was assumed that added ammonium-nitrogen would be biologically oxidized to nitrate-nitrogen during this oxidized period and would thus be available for subsequent denitrification under anaerobic conditions. The data summarized in Table B-3 indicate that three days after the moisture level was increased to 50% and carbon source was added, 21.27 to 33.06 mg nitrogen-15 gas was measured in the sealed chamber. The production of labelled nitrogen gas, as a consequence of

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denitrification of nitrate-nitrogen peaked at 8, 11, and 3 days after the increase in moisture levels to 50% in the 100 μ g nitrogen, 150 μ g nitrogen and 200 μ g nitrogen/g of soil added labelled ammonium-nitrogen treatments, respectively. A small increase in 44 and 45 mass/electron peak heights in the mass spectrometric analysis after the absorption of carbon dioxide gas suggests the evolution of nitrous oxide as a denitrification product. However, the levels of nitrous oxide produced were too small to give any significant numerical value.

The evolution of nitrogen gas during the second reduction cycle was very small and the maximum recovery in various ammonium-nitrogen treatments in the Mhoon-soil ranged from 4.61 to 8.41 mg nitrogen-15 and peaked at three to eight days after the commencement of the second reduction cycle (Table B-3). The nitrogen gas evolved during the two reduction cycles expressed as mg nitrogen-15 gas/cubic meters are graphically presented in Figure 12.

An inconsistent increase in nitrogen gas with time in some treatments in the enclosed atmosphere and a subsequent decrease in the concentration of nitrogen gas detected (Figure 12) may warrant some explanation. Nonuniform mixing of the evolved nitrogen gas in the enclosed atmosphere may be a reason for the fluctuating levels of nitrogen gas determined. The gas sampling port was located at the top of the desiccator assembly and no fan was installed to uniformly mix the sealed gaseous atmosphere before sampling. Some algal growth was observed in the desiccator when sealed under 50% soil moisture which may have fixed some evolved nitrogen gas and settled at the desiccator bottom with the condensed water causing a decrease in the labelled nitrogen gas levels inside the sealed atmosphere.

Significant levels of labelled nitrogen gas originating from the ammonium-nitrogen added at the start of the experiment confirm the occurrence of nitrification and denitrification processes. Ammonium-nitrogen added to the soil-plant system may have biologically oxidized to nitrate-nitrogen under oxidized conditions when the soil moisture was adjusted to about field moisture capacity. The increased soil moisture levels along with the addition of easily available energy source may have decreased redox potential to levels at which nitrates are unstable and resulted in the biological reduction of nitrates to nitrous oxide and nitrogen gases. The sequential occurrence of nitrification and denitrification may be responsible in the partial removal of nitrogen during land application of wastewater.

Mass Balance of Labelled Ammonium-Nitrogen Applied to Mhoon-Soil Rice System--

The soil mass and the plant shoots and roots were analysed for labelled nitrogen at the end of two oxidation/reduction cycles. A mass balance of applied nitrogen recovered in various system components is presented in Table 12. The uptake of

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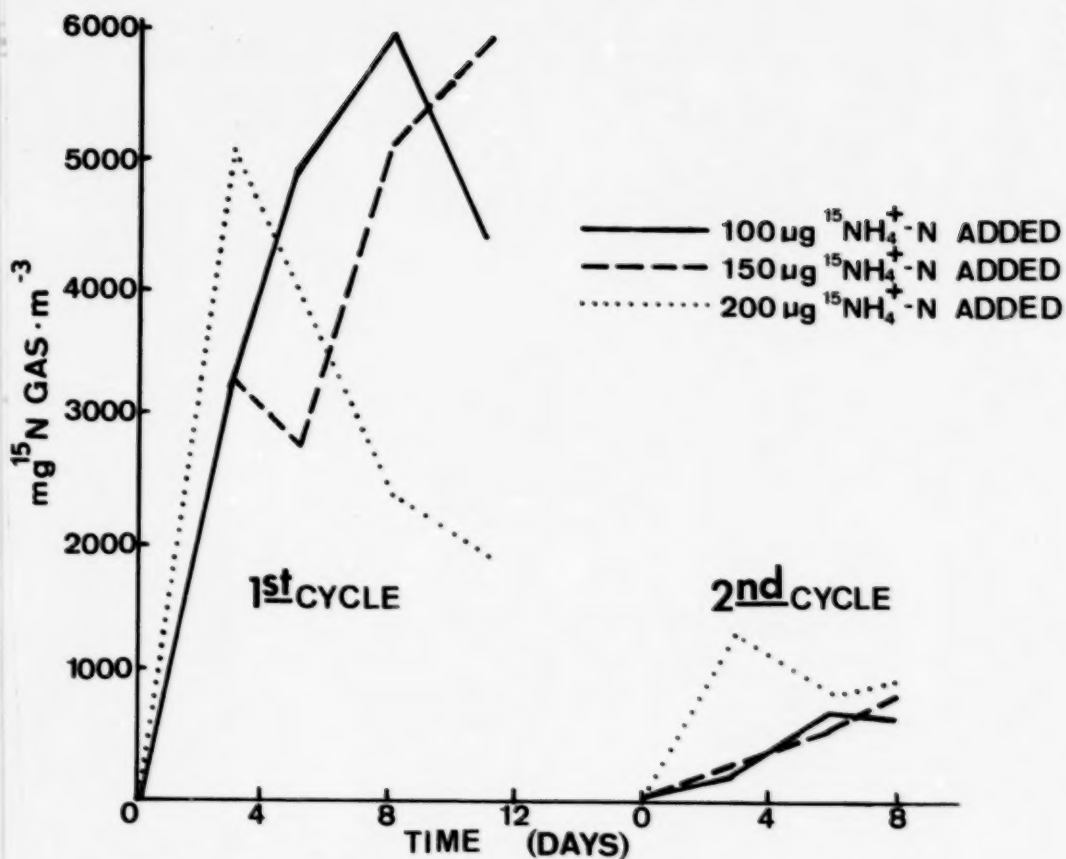


Figure 12. Effect of ammonium-nitrogen concentration on nitrogen-15 gas production measured in sealed atmosphere during two reduction cycles in Mhoon soil-rice system.

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TABLE 12. MASS BALANCE OF LABELLED AMMONIUM-NITROGEN ADDED TO
MHOON SOIL-RICE SYSTEM IN A SEALED GROWTH CHAMBER

System component	NH ₄ ⁺ - ¹⁵ N added					
	100 μg/g		150 μg/g		200 μg/g	
	¹⁵ N recovered					
	mg N	% of added	mg N	% of added	mg N	% of added
NH ₄ ⁺ added	152.20	100	228.30	100	304.40	100
Plant uptake	17.70	11.21	25.50	11.17	27.12	8.91
Soil fraction						
NH ₄ ⁺ -N	7.98	5.24	7.08	3.10	8.27	2.72
NO ₃ ⁻ -N	7.08	4.65	9.21	4.03	21.22	6.97
Organic N	38.42	25.24	57.34	25.12	69.84	22.94
Total N recovered	70.55	46.34	99.13	43.42	126.44	41.54
N loss	81.65	53.66	129.17	56.58	177.96	58.46

Incomplete recovery						
N ₂ gas	44.08	(28.96)	44.05	(19.29)	41.47	(13.62)
N ₂ O gas	trace	—	trace	—	trace	—
NH ₃ gas	1.05	(0.69)	2.30	(1.01)	2.85	(0.94)

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labelled nitrogen by rice plants as accounted for 8.91 to 11.21% of added labelled nitrogen. The soil fraction contained 32.25 to 35.13% of added ammonium-nitrogen. A larger fraction of this soil nitrogen was in the organic form which ranged from 22.94 to 25.24%. A significant portion of ammonium-nitrogen that was nitrified during the course of the experiment especially in the higher ammonium-nitrogen treatments was still present in the nitrate-nitrogen form and did not lose to the atmosphere due to denitrification or immobilization to organic fraction.

A balance sheet calculated for the added labelled nitrogen indicates that only 41.54 to 46.34% was recovered in the plant and soil fractions. This means that 53.66 to 58.46% of added labelled nitrogen was unaccounted. This nitrogen fraction may have been lost to the atmosphere through denitrification reactions or ammonia volatilization.

The recovery of added nitrogen present as nitrogen gas in the sealed atmosphere was calculated by adding together the highest value from each of the two reduction cycles and was assumed to be the maximum loss measured during the experimental period. The quantitatively measured denitrification loss as nitrogen gas accounted from 13.63 to 28.96% of applied labelled nitrogen. The proportion of applied nitrogen through ammonia volatilization was very small and accounted for only 1% of the total nitrogen.

The results indicate that more than 50% of applied nitrogen was lost from the soil-plant system due to denitrification reaction during two oxidation/reduction cycles. Fraction of this loss was not accounted for in the gaseous nitrogen analysis possibly due to incomplete mixing of labelled nitrogen in the sealed chamber or due to nitrogen fixation by algal growth in the desiccator assembly. Although an increase in the concentration of ammonium-nitrogen added to the system resulted in a greater amount of nitrogen lost from the system, the relative loss to ammonium-nitrogen added (53.66 to 58.46%) was fairly constant.

Comparative Nitrogen Loss from Applied Ammonium-Nitrogen in Mhoon and Grenada Soils in a Sealed Growth Chamber--

The data summarized in Table 13 give the distribution of added nitrogen in various system components. It should be pointed out that undisturbed soil cores with established rye grass and other plant species were used for Grenada soil in this study. Mhoon soil was packed in the plexiglas containers and rice plants were grown for a few weeks before the start of the experiment. The data indicate that a much larger fraction of added nitrogen was taken up by plants in Grenada soil compared to Mhoon soil (38.93 to 11.17% ¹⁵N). Also the added nitrogen remaining in the soil fraction as ammonium-nitrogen was five times greater in Grenada soil than that in Mhoon soil. This

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TABLE 13. COMPARISON OF ADDED LABELLED AMMONIUM-NITROGEN
(228.3 mg ^{15}N ; 150 $\mu\text{g N/g soil}$) RECOVERY BETWEEN MHOON SOIL-RICE
SYSTEM AND GRENADA SOIL-RYE GRASS SYSTEM IN A
IN A SEALED GROWTH CHAMBER

System components	Mhoon soil (pH 7.3)		Grenada soil (pH 6.9)	
	mg ^{15}N	^{15}N recovered % of added	mg ^{15}N	% of added
Plant uptake	25.50	11.17	88.89	38.93
Soil fraction				
$\text{NH}_4^+\text{-N}$	7.08	3.10	36.96	16.19
$\text{NO}_3^-\text{-N}$	9.21	4.03	3.76	1.65
Organic N	57.34	25.12	49.57	21.71
Total N recovered	99.13	43.42	179.18	78.48

Incomplete recovery				
N_2 gas	(44.05)	(19.29)	(5.97)	(2.61)
N_2O gas	trace	—	trace	—
NH_3 gas	(2.30)	(1.01)	(7.50)	(3.28)

* Grenada soil used in this study was collected from U.S. Army, CE Waterways Experiment Station's Overland Flow Research Facility at Utica, Mississippi. Details of sample collection are described in Experiment 5.

suggests that nitrification process may be a limiting factor in the Grenada soil. The mass balance of added ammonium-nitrogen calculated at the end of two oxidation/reduction cycles shows that 56.58 and 21.52% of added nitrogen was lost from the system in the Mhoon and Grenada soils, respectively. This greater gaseous nitrogen loss of applied ammonium-nitrogen in Mhoon soil was supported by the gas analysis of denitrification products by mass spectrometer. Maximum recovery of labelled nitrogen gas during two reduction cycles was 19.29% for Mhoon soil and 2.61 for Grenada soil (Table 13). The loss of labelled nitrogen as ammonia gas was slightly higher in Grenada than in Mhoon soil although the pH of Mhoon soil was more alkaline. Greater plant uptake and less nitrification potential of Grenada soil may be partially responsible for lower gaseous nitrogen loss than in Mhoon soil.

EXPERIMENT 5: A STUDY OF GASEOUS NITROGEN LOSSES OF APPLIED NITROGEN IN SEALED GROWTH CHAMBER SYSTEM IN GRENADA SOIL CORES COLLECTED FROM U.S. ARMY WATERWAYS EXPERIMENT STATION'S OVERLAND FLOW RESEARCH FACILITY, UTICA, MISSISSIPPI.

The main objective of this controlled laboratory experiment was to establish the relative contribution of gaseous nitrogen losses as a result of denitrification and ammonia volatilization processes in an already established overland flow treatment facilities for municipal waste water renovation. Waterways Experiment Station, Corps of Engineers, Overland Flow Treatment Facility at Utica, Mississippi was established to demonstrate pollutants removal efficiency of overland flow system on a long-term basis. The two years data published recently (Lee and Peters, 1978; Peters and Lee, 1978) indicated that 80% or more of nitrogen present in the applied lagoon effluent was removed by the overland flow treatment. Nitrogen removal efficiency of 94% was also reported in a prototype overland flow treatment experiment established in Hanover, New Hampshire where primary municipal effluent was applied in warmer months (Jenkins et al., 1978). It is suggested that in addition to plant uptake and microbial incorporation, gaseous nitrogen loss of applied nitrogen may be a significant factor in nitrogen removal of municipal effluent. Denitrification and ammonia volatilization potential of soil-plant system established at Utica, Mississippi were investigated in this experiment.

Experimental Procedures

Collection & Pretreatment of Soil Core Samples--

Undisturbed soil cores were collected from the U.S. Army CE, Waterways Experiment Station Overland Flow Experiment, Utica, Mississippi (courtesy of Dr. C. R. Lee of Waterways Experiment Station, Corps of Engineers, Vicksburg, Miss.) and transferred to plexiglas cylindrical containers (described in

Experiment 4 earlier). The soil cores was about 8-cm in depth, ($\approx$ 1500 g of oven dry soil) and had a good stand of mixture reed canary (*Phalaris arundinacea* L.), perennial rye grass and common Bermuda grass. The dominant plant species growing were of rye grass and therefore the system will be referred to as rye grass system. Plants were cut to a height of 5-cm and a pretreatment application of 100 μ g nitrogen/g of soil as unlabelled ammonium sulfate was made to all soil cores. Soil moisture in the soil-plant system was maintained at 25 to 30% level and the plants were grown in a cycle of 16 hours of light and eight hours of darkness for four weeks prior to nitrification-denitrification and ammonia volatilization studies.

Nitrification-Denitrification Study--

The nitrogen treatments applied to the soil-plant system, the duration of oxidation and reduction cycles after the nitrogen treatments were made, sampling sequence for various treatments, and duration for which the sealed atmosphere was monitored for denitrification products are summarized in Table 14.

After various nitrogen treatments were added, the moisture in the soil-plant system was maintained at 25% level to facilitate nitrification of added ammonium-nitrogen. Twenty-two days after the initial treatments were added, one of the ammonium-nitrogen-15 treatments (treatment E; Table 14) was removed and the soil was extracted with 2 N potassium chloride for analysis of ammonium- and nitrate-nitrogen to check the occurrence of nitrification process. After the soil-plant system was maintained under oxidized conditions for 31 days, the moisture content of the soil was increased to 50% and 50 μ g soluble carbon/g of soil was added to create reduced soil conditions and to provide energy source for denitrifying microorganisms. The soil-plant containers were transferred to the desiccator assembly described in Figure 11. The traps for hydrogen sulfide, carbon dioxide and ammonia gases were provided as described in Experiment 4. The desiccator assembly was sealed air-tight and was placed under 24 hour lights. The enclosed gaseous atmosphere was analysed by a mass spectrometry for nitrogen and nitrous oxide gases at regular intervals.

The sealed desiccators were opened and the soil-plant system was maintained at 25% moisture level to provide favorable conditions for the nitrification of remaining ammonium-nitrogen to occur. Treatment D was analysed for ammonium- and nitrate-nitrogen 18 days after the second oxidation cycle started. Twenty-eight days after the second oxidation cycle started, moisture level in the Treatments A, B, and C were raised to 50%, soluble carbon was added at the rate of 50 μ g C/g to each treatment and soil-plant containers were sealed in the desiccator assembly. The enclosed gaseous atmosphere was analysed for the next 12 days to monitor for the occurrence of denitrification of nitrate-nitrogen accumulated during the oxidation cycle.

TABLE 14. NITROGEN-15 TREATMENT APPLICATIONS TO GRENADA SOIL-
RYE GRASS SYSTEM, DURATION OF OXIDATION AND REDUCTION CYCLES,
AND SAMPLING SCHEDULE

Treatment code	$\text{NO}_3^-^{15}\text{N}^*$	$\text{NH}_4^+^{15}\text{N}^{**}$				
	A	B	C	D	E	
<u>Oxidation cycle 1</u>						
Moisture level, %	25	25	25	25	25	
Time, days (system open)	31	31	31	31	22	
Soil sampling	No	No	No	No	Yes	
<u>Reduction cycle 1</u>						
Moisture level, %	50	50	50	50	--	
Cumulative time, days (system sealed)	44	44	44	44	--	
Gas sampling	Yes	Yes	Yes	Yes	--	
<u>Oxidation cycle 2</u>						
Moisture level, %	25	25	25	25	--	
Cumulative time, days (system open)	72	72	72	62	--	
Soil sampling	No	No	No	Yes	--	
<u>Reduction cycle 2</u>						
Moisture level, %	50	50	50	--	--	
Cumulative time, days (system sealed)	84	84	84	--	--	
Gas sampling	Yes	Yes	Yes	--	--	
Soil and plant sampling at the end of 84-day experiment	Yes	Yes	Yes	--	--	

* 600 mg $\text{NO}_3^-^{15}\text{N}$ (56.609 atom % ^{15}N) as KNO_3 was applied at the beginning of oxidation cycle 1.

** 600 mg $\text{NH}_4^+^{15}\text{N}$ (49.664 atom % ^{15}N) as $(\text{NH}_4)_2\text{SO}_4$ was applied to each treatment at the beginning of oxidation cycle 1. The applied nitrogen is equivalent to 400 μg N/g soil.

The experiment was then terminated and various soil and plant fractions were analysed for labelled nitrogen.

Ammonia Volatilization Study--

Unlabelled ammonium-nitrogen at the rate of 600 mg nitrogen/container (equivalent to 400 μ g nitrogen/g of soil) was added to two soil cores similar to the ones used for nitrification-denitrification study described.

Desiccator assembly described in Figure 11 was used for the ammonia volatilization study with provisions for an inlet and an outlet through the desiccator walls to force the enclosed atmosphere to pass through an acid trap. The air was passed through an acid trap containing 200 ml of 0.1 N sulfuric acid to absorb any ammonia present in the atmospheric air prior to entering the desiccator. The air stream from the sealed desiccator assembly was passed through a set of two acid traps with 100 ml of 0.1 N sulfuric acid in each trap to absorb ammonia gas evolved from the soil-plant system in the sealed desiccator. Fifty milliliters of 0.1 N sulfuric acid was placed in each desiccator to trap any ammonia gas volatilized and condensed with the cooling water.

Soil-plant cores were placed in each of the two desiccators and sealed. Air was passed through the desiccator assembly at the rate of 20 ml/minute. Ammonia absorbed by the acid traps was analysed at regular intervals. The ammonia volatilized during two oxidation/reduction cycles identical to treatments B and C in the nitrification-denitrification study (Table 14) were monitored. The experimental conditions maintained in this study were identical to treatments C and D in the nitrification-denitrification study.

Results and Discussion

Effect of oxidation/Reduction Cycles on Nitrification of Applied Ammonium-Nitrogen in Grenada Soil-Rye Grass System--

One of the objectives of this experiment was to monitor the occurrence of nitrification reaction when the soil moisture was maintained around 25% to create favorable conditions for the growth of nitrifiers. Twenty-two days after the ammonium-nitrogen was added to soil-plant system Treatment E (600 mg of ammonium-nitrogen-15 application) was extracted for ammonium- and nitrate-nitrogen. About 5% of added ammonium-nitrogen was present in the nitrate-nitrogen form which indicated the occurrence of nitrification process although at a slow rate (Table 15). At the end of the second oxidation cycle (62 days after the start of the experiment) 8.5% of added ammonium-nitrogen was determined in nitrate-nitrogen form. The fraction of nitrate-nitrogen accumulated at the end of the first oxidation cycle may not be reflected in the 8.5% determined at the end of the second oxidation cycle. The first oxidation cycle was

TABLE 15. EFFECT OF OXIDATION-REDUCTION CYCLES ON NITRIFICATION OF APPLIED AMMONIUM-NITROGEN IN GRENADA SOIL-RYE GRASS SYSTEM

Treatment code	E	D	Avg B + C
$\text{NH}_4^+ - ^{15}\text{N}$ applied, mg	600*	600*	600*
Oxidation/reduction cycle	Oxidation cycle 1	Oxidation/reduction cycle 1; Oxidation cycle 2	Oxidation/reduction - 2 cycles
Cumulative time, days	22	62	84
<u>Applied ^{15}N recovered, mg</u>			
$\text{NH}_4^+ - \text{N}$	234.87	194.88	123.68
$\text{NO}_3^- - \text{N}$	31.50	50.83	24.26

* 600 mg ^{15}N applied is equivalent to 400 $\mu\text{g N/g}$ soil.

followed by a reduction cycle where soil moisture was increased to 50% to create favorable conditions for the denitrification of nitrate-nitrogen accumulated. Following a 13-day reduction cycle (Table 14) soil moisture was maintained at 25% to allow nitrification of ammonium-nitrogen still present in the system. The nitrate-nitrogen (8.5%) accumulated at the end of 62 days may reflect the conversion of added ammonium- to nitrate-nitrogen. Only 4% of total ammonium-nitrogen added was in the nitrate-nitrogen form at the end of the 84-day experiment (Table 15, Treatments B & C). A large fraction of ammonium-nitrogen applied at the start of the experiment remaining in the ammonium-nitrogen form (123.68 mg nitrogen; 20.6% of added nitrogen) strongly indicates that the nitrification rate was not very high in this soil. Since nitrification of ammonium-nitrogen through denitrification processes, the nitrification process in this soil would thus be a limiting factor.

Measurements of Denitrification Products During Two Reduction Cycles in Grenada Soil-Rye Grass System in a Sealed Chamber--

Soil moisture level in the soil-plant system was maintained at 25% for 31 days to facilitate biological oxidation of added ammonium-nitrogen (Treatments B & C, Table 14). The moisture level was then increased to 50% and soluble carbon was added to both nitrate- and ammonium-nitrogen treatments. The soil-plant system was sealed in the desiccator assembly and the evolution

of nitrogen and nitrous oxide gases or as a result of biological denitrification of nitrate-nitrogen was measured at regular intervals for the next 13 days. The nitrogen gas data plotted in Figure 13 indicate that maximum concentration of labelled nitrogen gas was observed on the fourth day after the system was sealed. A sharp drop in nitrogen gas was observed at the sixth day of sampling and the levels fluctuated slightly thereafter. No difference in the concentration of nitrogen gas detected in the nitrate- and ammonium-nitrogen treatments was observed in the first reduction cycle.

In the second reduction cycle which followed the second oxidation cycle and commenced on the 73rd day after the initial treatments were applied, the concentration of labelled nitrogen gas peaked to maximum values on the seventh day after the system was sealed. This highest concentration of labelled nitrogen gas as a result of denitrification was observed in both nitrate- and ammonium-nitrogen treatments. The concentration of nitrogen gas then dropped and subsequently levelled off. The concentration of nitrogen gas in the sealed chamber in the nitrate-nitrogen treatment observed in the second reduction cycle was almost twice as high as in the ammonium-nitrogen treatment. The total labelled nitrogen gas evolved during the two reduction cycles expressed as mg nitrogen-15 gas/treatment is summarized in Table B-4. No measurable nitrous oxide gas was detected in the mass spectrometric analysis in this experiment.

Mass Balance of Labelled Ammonium- and Nitrate-Nitrogen Applied to Grenada Soil-Rye Grass System--

The soil mass and the plant roots and shoots were analysed for labelled nitrogen at the end of two oxidation/reduction cycles. The maximum recovery of labelled nitrogen gas in the sealed atmosphere was calculated by adding together the highest concentration of nitrogen gas from each of the two reduction cycles. The contribution of ammonia volatilization from added ammonium-nitrogen was determined from an identical experiment conducted under similar conditions but with provisions to constantly trap evolved ammonia gas. These data are summarized in Table 16.

The data presented in Table 16 show that slightly more labelled nitrogen was taken up by plants in the nitrate-nitrogen treatment than in the ammonium-nitrogen treatment (24.75 vs 20.34% respectively). The proportion of added nitrogen recovered in the soil fraction was three times higher in the ammonium-nitrogen treatment than that in the nitrate-nitrogen treatment. The residual ammonium-nitrogen present in soil complex at the end of 84 days was 20.61% in the ammonium-nitrogen treatment. This strongly suggests that the biological oxidation of ammonium- to nitrate-nitrogen was limited in Grenada soil. The nitrate-nitrogen accumulation in the soil fraction was small and

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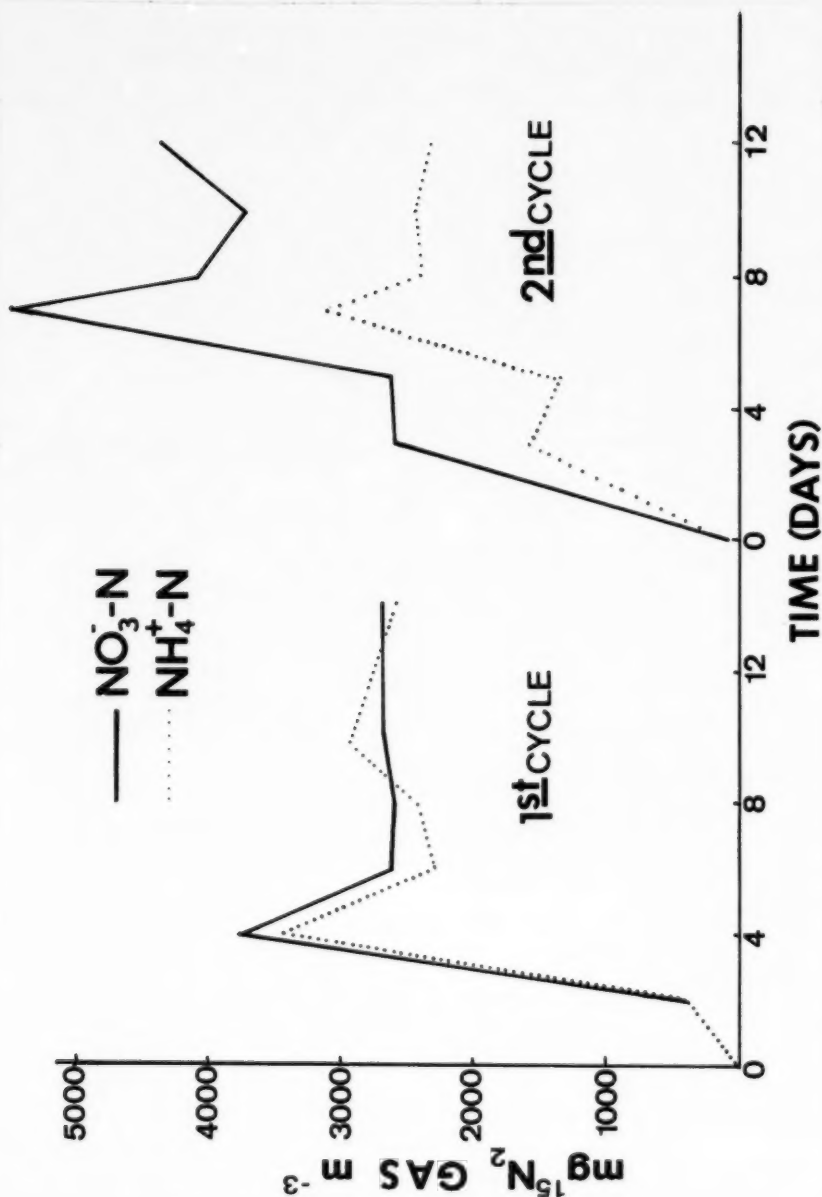


Figure 13. Effect of nitrogen forms on nitrogen-15 gas production as measured in sealed atmosphere during two reduction cycles in Grenada soil-rye grass system.

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TABLE 16. MASS BALANCE OF LABELLED AMMONIUM- AND NITRATE-NITROGEN ADDED TO GRENADA SOIL-RYE GRASS SYSTEM IN A SEALED GROWTH CHAMBER

System component	N treatment				% of added N
	NO ₃ ⁻ -N		NH ₄ ⁺ -N		
	mg N	% of added N	15N recovered		
N added	600	100	600		100
Plant uptake	148.53	24.75	122.06		20.34
Soil fraction					
NH ₄ ⁺ -N	0.69	0.11	123.68		20.61
NO ₃ ⁻ -N	14.84	2.47	24.26		4.04
Organic N	83.30	13.88	128.13		21.35
Total N recovered	247.36	41.21	398.13		66.34
N loss	352.64	58.79	201.87		33.66
Gaseous recovery					
N ₂ (incomplete)	60.56	10.09	43.09		7.18
N ₂ O (incomplete)	traces	0.00	traces		0.00
NH ₃	--	--	29.55		4.92
N not accounted for	--	48.70	129.23		21.56

accounted for only 2.47 and 4.04% at the end of experiment in the nitrate- and ammonium-nitrogen treatments, respectively.

The total recovery of labelled nitrogen in the soil and plant fractions accounted for 41.21 and 66.34% in the nitrate- and ammonium-nitrogen treatments, respectively. This means that 58.79% of added nitrate- and 33.66% of added ammonium-nitrogen was lost to the atmosphere during 84 days of experiment. The greater loss of nitrate-nitrogen is thought to be primarily due to only denitrification reaction. In the case of ammonium-nitrogen, nitrification reaction must precede the denitrification process. In this experiment, the incomplete oxidation of ammonium- to nitrate-nitrogen resulted in less nitrogen loss to the atmosphere.

The quantitative determination of labelled nitrogen gas in the sealed atmosphere accounted for a maximum of 10.09 and 7.18% recovery in the two reduction cycles in the nitrate- and ammonium-nitrogen treatments, respectively. Loss of ammonium-nitrogen due to ammonia volatilization accounted for only 5% of the total added. This means that 48.7% of added nitrate- and 21.56% of added ammonium-nitrogen were not accounted for in this experiment. The followings may be the possible pathways for this nitrogen loss:

1. Although the moisture level of 25% maintained during the oxidation cycles in the experiment may have created generally oxidized conditions, it is likely that redox potentials may have decreased to below nitrate stability zone resulting in the occurrence of denitrification process and hence in the nitrogen loss. Redox potentials were not measured in this experiment.

2. When the sealed system was opened after each reduction cycle the moisture content ranged between 25 to 35% and denitrification process may have still been occurring resulting in the nitrogen loss.

3. It is possible that algal growth in the sealed desiccators during the two reduction cycles may have fixed some gaseous nitrogen and settled at the bottom of the desiccator along with the condensing water; and

4. Nonuniform mixing of evolved labelled nitrogen gas in the desiccator atmosphere may have underestimated nitrogen gas recovery as the gas samples were taken from the top portion of the sealed desiccator.

In spite of the incomplete recovery of gaseous nitrogen in the enclosed atmosphere, the presence of significant amounts labelled nitrogen gas in both treatments demonstrate that gaseous nitrogen loss can be a significant nitrogen removal process in land treatment of wastewater.

EXPERIMENT 6. EFFECT OF NITROGEN FORMS AND PLANT GROWTH ON NITROGEN REMOVAL PROCESSES IN AN OVERLAND FLOW TREATMENT OF SIMULATED WASTEWATER.

Several research studies conducted on cropped soil, pasture or grassland soils have indicated a possible role of plant growth and live root mass on accelerated gaseous nitrogen losses in the soil. Woldendorp (1963) attributed the stimulating effect of living plants to denitrification at low oxygen tension in the rhizosphere to: (1) respiration of root system and the microflora and (2) root excretions serving as a source of hydrogen donors during denitrification. Using sealed plant growth chambers, Stefanson and Greenland (1970) showed a considerable increase in evolved nitrogen and nitrous oxide from the soil nitrogen in the presence of plants. In a later study, Stefanson (1973) found that losses of applied nitrogen through biological denitrification products of nitrogen and nitrous oxide gases increased substantially only when nitrogen was applied as nitrate. Plant growth did not affect the amount of nitrous oxide or nitrogen gas evolved from the soil receiving ammonium-nitrogen.

No studies have been reported on the role of rhizosphere in enhancing nitrogen removal from wastewater through gaseous losses in an overland flow system. The objectives of this research therefore were (1) to compare the loss of applied labelled nitrogen due to nitrification-denitrification and ammonia volatilization reactions in an overland system in Mhoon soil covered with rye grass plants and that without any plant growth, (2) to study the effect of ammonium- and nitrate-nitrogen forms and the relative distribution of applied labelled nitrogen in runoff, soil, plant, and atmospheric components in an overland flow system in Mhoon soil.

Experimental Procedure

Mhoon silt loam soil, limed with 60 meq of CaCO_3 /100 g of soil to raise the pH to ≈ 7.0 was used for this overland flow experiment. Air-dried soil (equivalent to 5.19 kg of oven dried) was uniformly packed to an 8-cm height in plexiglass test containers 50-cm in length, 10-cm in depth (illustration similar to Figure 1). The overland flow test container was constructed of a 0.63-cm thickness of plexiglass. To activate microbial population necessary for nitrogen transformations, 700 ml of lagoon water, 30 μg phosphorus/g soil, and 100 μg carbon/g soil was added to each test container and the soil was equilibrated for four weeks at 35% moisture. After the four-week equilibration period, 10 g of rye grass seed were sprinkled uniformly on soil surface in two of the test containers. After the seedlings were 10 days of age, the test containers with and without plants were placed on 1.2% slope, and 14 hours of light and 10 hours of darkness was provided for normal plant growth. Platinum

electrodes were installed at 2-cm and 4-cm depths, in duplicate, in each test container to monitor redox potential. A pretreatment application of 775 ml of tap water (equivalent to 1.5 cm water/day) containing 75 μg soluble carbon/ml was applied to each test container on alternate days for two weeks to test water flow patterns and to create more natural conditions.

Nitrogen Treatment Applications to Overland Flow Model--

Four treatment combinations summarized below were studied in this overland flow experiment:

- Treatment 1. 40 μg $^{15}\text{NH}_4^+$ -N/ml without plants.
- Treatment 2. 40 μg $^{15}\text{NH}_4^+$ -N/ml with rye grass plants.
- Treatment 3. 40 μg $^{15}\text{NO}_3^-$ -N/ml without plants.
- Treatment 4. 40 μg $^{15}\text{NO}_3^-$ -N/ml with rye grass plants.

Soluble carbon at the rate of 75 μg carbon/ml was also added with each influent application in these treatments. Labelled ammonium-nitrogen was applied as ammonium sulfate (10.316 atom % nitrogen-15) and labelled nitrate-nitrogen as potassium nitrate (10.284 atom % nitrogen-15). Treatments 1 and 2 also received 110 μg potassium/ml as potassium chloride to raise potassium levels to that in Treatments 3 and 4.

The 775 ml influent solutions equivalent to 1.5-cm of water/day containing nitrogen treatments were applied to overland flow test containers at the rate of 1.3 ml/minute for 10 hours per day on alternate days. The combined runoff plus sub-flow effluent was analysed for ammonium- and nitrate-nitrogen at the end of each application. Redox potential measurements were recorded daily. A total of 13 overland flow nitrogen applications were made to test models during the 26-day experimental period. This was followed by two applications of distilled water to all four treatments made on alternate days prior to termination of the experiment.

Soil and Plant Analysis--

The plants harvested at the end of the experiment were digested and analysed for labelled nitrogen. Soil mass in the test containers was sectioned to 0- to 12.5-, 12.5- to 25-, 25- to 37.5- and 37.5- to 50-cm lengths downslope. Each soil section was then divided to 0- to 4- and 4- to 8-cm soil depths. Soil samples were analysed for labelled ammonium-, nitrate- and organic-nitrogen fractions. A mass balance of applied labelled nitrogen in various runoff, soil, and plant components was calculated and gaseous loss of applied nitrogen was determined.

The pH of soil samples collected at the end of the experiment was measured in 1:2 soil-water ratio. All soil and plant analyses were conducted in duplicate and average data are reported.

Results and Discussion

Redox Potential Measurements During Overland Flow Treatment--

The redox potentials were measured at 2-cm and 4-cm depths to determine the oxidation-reduction status of near-surface and subsurface soil layers. Redox potential values measured in the ammonium- and nitrate-nitrogen treatments both with plants growing are presented in Figure 14. Since the data for treatments without plants were similar to that with plants growing, these are not plotted. The redox potential values generally oscillated between +600 mv to 0 mv and occasionally dropped to as low as -170 mv. The redox potential values recorded at the 2-cm depth were generally slightly higher than those at 4-cm depth. The range of redox potential values for ammonium- and nitrate-nitrogen treatments with or without plants were similar and no drastic treatment effects were noted.

It is evident from Figure 14 that well oxidized conditions were present at 2-cm depth as well as 4-cm depths to allow biological oxidation of added ammonium-nitrogen. The redox potential value generally decreased to below 350 mv (at which nitrate-nitrogen is unstable) following the influent application and then increased to more oxidized levels until the next influent application was made. The presence of both oxidized and reduced zones identified in the overland flow system may facilitate simultaneous nitrification and denitrification processes and enhance gaseous nitrogen loss (Broadbent and Tusneem, 1971; Reddy, 1976).

Mass Balance of Influent Ammonium- and Nitrate-Nitrogen Applied to Mhoon Soil in an Overland Flow Model--

The combined runoff and subflow collected from various treatments at the end of each influent application was analysed for labelled ammonium- and nitrate-nitrogen to determine the nitrogen removal efficiency of overland flow system. The data on the recovery of labelled ammonium- and nitrate-nitrogen in the effluents are summarized in Table B-5. The results show that an insignificant fraction of applied nitrogen was recovered in the runoff plus subflow effluents which indicates an essentially complete retention of applied nitrogen by the soil or soil-plant system.

A mass balance of added labelled nitrogen recovered in the runoff plus subflow, soil and plant components is summarized in Table 17. The data indicate that only 0.82 to 1.98% of added nitrogen was recovered in the runoff plus subflow fractions in various treatments. The fraction of nitrate-nitrogen present

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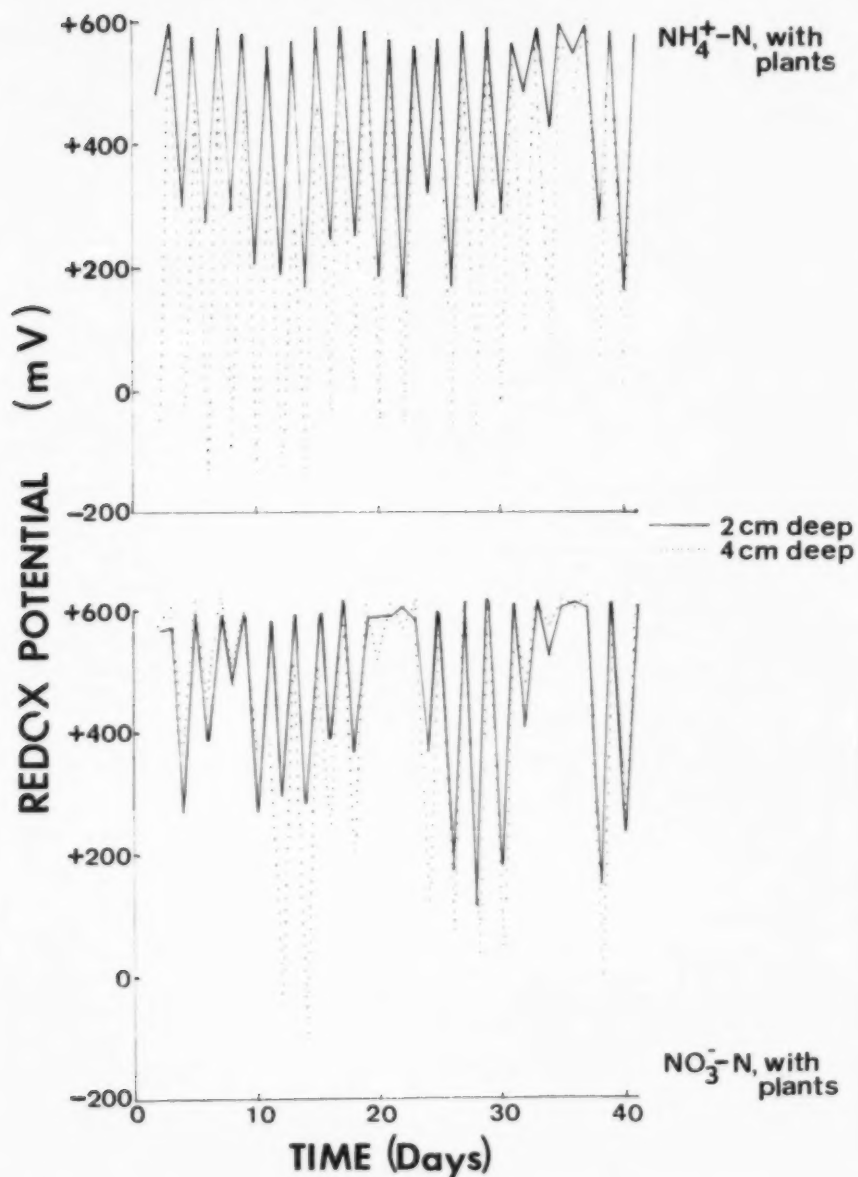


Figure 14. Effect of nitrogen forms on redox potentials measured at two soil depths during overland flow treatment of simulated wastewater.

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TABLE 17. EFFECT OF NITROGEN FORMS AND PLANT GROWTH ON DISTRIBUTION OF APPLIED LABELLED NITROGEN IN VARIOUS COMPONENTS IN MHOON SOIL OVERLAND FLOW MODEL

System component	Treatments						
	$\text{NH}_4^+\text{-N}$			$\text{NO}_3^-\text{-N}$			
	without plants	with plants	^{15}N Recovered	without plants	with plants	% of added N	% of added N
	mg N	mg N	% of added N	mg N	mg N	% of added N	mg N
Total N Added	387.29	100	387.29	100	406.46	100	406.46
Runoff & Subflow							100
$\text{NH}_4^+\text{-N}$	3.13	0.81	5.11	1.32	1.43	0.35	0.47
$\text{NO}_3^-\text{-N}$	0.06	0.01	0.15	0.04	6.61	1.63	4.36
Soil							1.07
$\text{NH}_4^+\text{-N}$	2.42	0.62	4.02	1.04	1.50	0.37	1.56
$\text{NO}_3^-\text{-N}$	2.42	0.62	5.74	1.48	1.17	0.29	0.95
Organic N	262.19	67.67	183.34	47.34	193.27	47.55	150.08
Plants							36.92
shoots	--	--	86.33	22.29	--	--	31.03
roots	--	--	8.72	2.25	--	--	6.53
Total N recovered	270.22	69.73	293.41	75.76	203.98	50.19	194.98
N loss	117.07	30.27	93.88	24.24	202.48	49.81	211.48
							52.05

in the effluent samples in ammonium-nitrogen treatments was negligible and no effect of plant growth was observed. Similarly, very little ammonium-nitrogen produced from nitrate-nitrogen reduction was transported with effluent waters in the nitrate-nitrogen treatments.

The fraction of added nitrogen retained by the soil complex ranged from 37.53 to 68.91% in various treatments and most of this soil nitrogen was present in the organic-nitrogen fraction. Very little of the added nitrogen was present in the ammonium- or nitrate-nitrogen fraction in any of the treatments. The ammonium- and nitrate-nitrogen recovery in the added ammonium-nitrogen treatments was slightly higher where plants were growing than that in the bare soil. No effect of rhizosphere on inorganic nitrogen fractions in the nitrate-nitrogen treatments was noticed.

Considerably more ammonium-nitrogen was transformed into the organic form in the ammonium-nitrogen treatment without plants compared to that with plants growing (67.67 vs. 47.34%). This difference in the immobilization of added ammonium-nitrogen by the organic fraction was mainly due to plant uptake of added nitrogen where 24.54% of added ammonium-nitrogen was recovered in the plant shoots and roots. Similarly, more added nitrate-nitrogen was assimilated in the organic fraction in the absence of plants than in the treatments with rye grass (Table 17). The fraction of added nitrate-nitrogen not recovered in the organic fraction in the treatment with plants was taken up by the growing plants and accounted for 9.24% of added nitrate-nitrogen.

The data presented in Table 17 show that a greater proportion of added nitrogen was transformed into the organic fraction and/or taken up by the plants in the ammonium than in the nitrate-nitrogen treatments. It is likely that the presence of favorable conditions in the overland flow experiment (low redox potential and easily available energy source) resulted in a competition between nitrate assimilation and denitrification in the nitrate-nitrogen treatments. Also, preferential uptake by rye grass plants of ammonium-nitrogen over nitrate-nitrogen may have resulted in greater uptake of ammonium-nitrogen than nitrate-nitrogen. Similar effects of nitrogen forms on nitrogen immobilization and on preferential uptake of added nitrogen have been reported in Olivier soil-rye grass system discussed in Experiment 7 (Table 20).

The mass balance of labelled nitrogen added to Mhoon soil overland flow model during the 30-day experiment shows that 24.24 to 30.27% of added ammonium- and 49.81 to 52.05% of added nitrate-nitrogen were lost from the system. It is evident that nitrogen loss from the nitrate-nitrogen treatments was about two

orders of magnitude greater than ammonium-nitrogen treatments. The effect of plant growth on nitrogen loss was relatively small and variable. For example, in the ammonium-nitrogen treatment more nitrogen was lost from the overland flow model with no plant growth than with rye grass growing. The effect of plant growth in the nitrate-nitrogen treatments was in the reverse order.

The fraction of applied nitrogen not recovered in the overland flow model may have been lost to the atmosphere through ammonia volatilization (only in ammonium-nitrogen treatments) and denitrification reactions. The alkaline soil conditions in various treatments (See Table B-6 for soil pH values) may favor ammonia volatilization losses in this experiment. However, in Experiment 4, described earlier where similar quantities of calcium carbonate were added to raise the soil pH, only about 1% of added ammonium-nitrogen was lost through ammonia volatilization in Mhoon soil (See Table 12). The results of this overland flow model suggest that significant quantities of applied nitrogen can be removed through gaseous nitrogen production under conditions favorable for the simultaneous nitrification and denitrification reactions. The effect of rhizosphere on gaseous nitrogen loss of applied nitrogen was not evident in this experiment.

Distribution of Labelled Soil Nitrogen Fraction as a Function of Soil Depth and Downslope Length--

The fraction of applied nitrogen removed by the soil in the ammonium-, nitrate- and organic-nitrogen fractions at the end of the experiment was determined in the 0- to 4- and 4- to 8-cm depths sectioned with slope. The data are presented in Tables 18 and 19 for ammonium- and nitrate-nitrogen treatments, respectively. Ammonium-, nitrate-, and organic-nitrogen decreased sharply with slope and this effect was evident in all treatments under study. A consistent decrease in labelled nitrogen with depth was observed in 0- to 12.5-cm and 12.5- to 25.0-cm sections downslope. The effect of depth and slope distance was much greater in organic-nitrogen fraction than in the ammonium- or nitrate-nitrogen fractions. In the ammonium-nitrogen treatments more nitrogen was transformed to the organic fraction in the overland flow model without plants than that with plants growing and this effect was evident at both soil depths and at all points downslope (Table 18). In the nitrate treatments, the effect of plant growth in decreasing the fraction of labelled nitrogen incorporated in the organic fraction was evident only in the surface soil layer at various points downslope (Table 19).

The results of this study show that growing plants significantly affected only the pool of organic nitrogen and did not increase the loss of applied nitrogen through denitrification reactions.

TABLE 18. EFFECT OF PLANT GROWTH ON THE DISTRIBUTION OF APPLIED AMMONIUM-NITROGEN IN VARIOUS SOIL FRACTIONS IN MHOON SOIL DETERMINED AT THE END OF OVERLAND FLOW TREATMENTS

Depth cm	NH ₄ ⁺ -N, without plants					NH ₄ ⁺ -N, with plants				
	Distance downslope, cm									
	0-12.5	12.5-25	25-37.5	37.5-50	0-12.5	12.5-25	25-37.5	37.5-50	0-12.5	12.5-25
	NH ₄ ⁺ -N, μ g ¹⁵ N									
0-4	558	226	100	319	2149	363	200	116		
4-8	460	203	116	435	787	166	110	137		
	NO ₃ ⁻ -N, μ g ¹⁵ N									
0-4	853	264	114	123	2239	731	343	149		
4-8	369	333	187	180	1147	621	248	266		
	Organic N, mg ¹⁵ N									
0-4	99.18	41.94	16.84	13.32	91.29	18.16	14.05	7.74		
4-8	43.40	24.36	10.07	13.08	23.93	12.18	8.60	7.39		

TABLE 19. EFFECT OF PLANT GROWTH ON THE DISTRIBUTION OF APPLIED NITRATE-NITROGEN IN VARIOUS SOIL FRACTIONS IN MHOON SOIL DETERMINED AT THE END OF OVERLAND FLOW TREATMENTS

Depth cm	NO ₃ ⁻ -N, without plants					NO ₃ ⁻ -N, with plants				
	Distance downslope, cm									
	0-12.5	12.5-25	25-37.5	37.5-50	0-12.5	12.5-25	25-37.5	37.5-50	0-12.5	12.5-25
	NH ₄ ⁺ -N, µg ¹⁵ N									
0-4	293	346	208	171	463	215	148	74		
4-8	170	100	148	61	223	187	151	102		
	NO ₃ ⁻ -N, µg ¹⁵ N									
0-4	221	196	201	104	171	192	73	61		
4-8	153	73	100	121	211	126	60	53		
	Organic N, mg ¹⁵ N									
0-4	68.60	24.71	23.01	17.20	62.35	16.29	6.67	6.63		
4-8	28.43	12.12	11.10	8.10	19.53	15.06	12.75	10.80		

EXPERIMENT 7. EFFECT OF NITROGEN FORMS ON THE KINETICS OF
NITROGEN LOSS IN SIMULATED WASTEWATER TREATMENT IN OLIVIER SOIL-
RYE GRASS SYSTEM

Nitrification-denitrification experiments discussed earlier in this section indicated that gaseous loss of applied nitrogen may be a significant process in the removal of nitrogen during land application of wastewater. A greater loss of applied nitrogen occurred when applied as nitrate-nitrogen than when applied as ammonium-nitrogen. However, the rate of nitrogen transformation and especially of nitrogen loss was not investigated in these experiments. The objective of this experiment was to study the kinetics of nitrogen loss applied as ammonium- and nitrate-nitrogen during an alternate anaerobic-aerobic cycle in Olivier soil-rye grass system as occurs in overland flow treatment of wastewater.

Experimental Procedures

Two hundred grams of Olivier soil limed with calcium carbonate to pH 6.5 were placed in 300 g capacity, 10-cm plastic containers and adjusted to 35% moisture for one week to allow the calcium carbonate to react with the soil. Rye grass seeds were evenly spread on soil surface at the rate of 0.5 g to each container and were covered until the seeds germinated. A blanket application of 100 μ g phosphorus and 50 μ g soluble carbon/g soil was added to each container. Rye grass seedlings were grown for 10 days at controlled moisture content of 20 to 35%.

Labelled ammonium- and nitrate-nitrogen [10.372 atom % nitrogen-15 as ammonium sulfate and 10.059 atom % nitrogen-15 as potassium nitrate] were applied at the rate of 50 μ g nitrogen/g of soil on the 1st, 7th, 13th, 18th, 22nd, 28th, and 33rd day. Twenty-five μ g carbon/g of soil was also applied with nitrogen treatments. After each nitrogen treatment addition, moisture level in the soil-plant system was adjusted to 55% and was then allowed to drop to 20% and was maintained at this level for 24 hours. This cycle of alternate flooding and drying was repeated one more time. At the end of every second cycle, duplicate samples were taken from each treatment in the experiment. Plant shoots and roots were washed, dried at 60°C and analysed for labelled nitrogen. Soil samples were analysed for labelled ammonium-, nitrate- and organic-nitrogen. The pH of soil samples collected at the end of two cycles was also determined. Nitrogen treatments were applied to the remaining soil-plant containers which were subjected to two alternate flooding and drying cycles. Various soil-plant components were then analysed for labelled nitrogen. Soil and plant samples were taken at the end of the 6th, 12th, 21st, 27th, 32nd, and 38th day after the start of the experiment and were analysed for labelled nitrogen. Loss of applied nitrogen due to ammonia volatilization and denitrification processes was determined by subtracting the nitrogen

recovered in the soil and plant components from that applied to the soil-plant system. Kinetics of nitrogen loss in the ammonium- and nitrate-nitrogen treatments were computed using a linear zero order kinetics model.

Results and Discussion

Data summarized in Table 20 show that the accumulation of added ammonium-nitrogen in the soluble plus exchangeable fractions increased as nitrogen additions were made with time. About 6.6% of added ammonium-nitrogen-15 was still present in the ammonium-nitrogen form at the end of 38 days. Essentially no residual nitrate was found in the soil during the length of the experiment as the maximum concentration determined at the end of the last nitrogen application was only 0.42 μg nitrate-nitrogen-15/g of soil. It is evident that unlike ammonium-nitrogen, the nitrate-nitrogen formed due to biological ammonium oxidation under oxidized soil conditions was very unstable and immediately transformed into other nitrogen forms.

The incorporation of added ammonium-nitrogen into the organic fraction increased with time in a linear mode and was several orders of magnitude greater than the residual ammonium-nitrogen fraction. This organic fraction plays an important role in the overland flow treatment system as a nitrogen sink thus reducing ammonium-nitrogen levels in the runoff waters. However, in the permanently established overland flow systems, the organically fixed nitrogen would mineralize with time and may be subject to recycling.

Labelled nitrogen applied as nitrate was not converted to ammonium-nitrogen or accumulated as nitrate-nitrogen to any significant levels as their concentrations remained below 1.0 μg nitrogen/g soil. The applied nitrate-nitrogen may have denitrified to nitrogen or nitrous oxide gases upon flooding, been taken up by the growing plants, or immobilized to organic-nitrogen. The analysis of organic-nitrogen fraction shows that 2.75 μg to 23.85 μg nitrogen-15/g of soil was incorporated with the organic fraction. Several mechanisms are proposed in the literature for the conversion of nitrate- to organic-nitrogen such as anoxic nitrate assimilation (MacRae et al., 1968; Chen et al., 1972) and respiratory reduction to ammonium- and organic-nitrogen (Stanford et al., 1975; Buresh and Patrick, 1978). The soil conditions conducive to substantial respiratory reduction of nitrate-nitrogen include excessive amounts of easily reducible carbon source and intense soil reduction. In wastewater treatment systems described in Experiment 3 and 6 in the study and others (Hoepfel et al., 1974; Carlson et al., 1974) the organic carbon source in the applied wastewater is generally low (< 100 mg carbon/l) and the redox potential values fluctuate between reduced and oxidized with alternate wetting drying cycles.

TABLE 20. EFFECT OF NITROGEN FORMS ON THE RECOVERY OF APPLIED LABELLED NITROGEN IN VARIOUS SOIL AND PLANT COMPONENTS

System components analyzed	Time, days					
	6	12	17	21	27	32
	50	100	150	200	250	300
			N applied; $\mu\text{g } ^{15}\text{N/g soil}$			
						350
			Applied $^{15}\text{NH}_4^+$ -N recovered, $\mu\text{g } ^{15}\text{N/g soil}$			
NH_4^+ -N	0.39	1.11	1.91	6.85	9.64	20.39
NO_3^- -N	0.08	0.09	0.08	0.19	0.23	0.26
Organic N	7.85	12.75	15.75	20.65	25.05	39.30
			Applied $^{15}\text{NO}_3^-$ -N recovered, $\mu\text{g } ^{15}\text{N/g soil}$			
NH_4^+ -N	0.10	0.20	0.53	0.65	0.66	0.51
NO_3^- -N	0.18	0.12	0.13	0.12	0.88	0.60
Organic N	2.75	5.10	8.80	11.35	14.50	19.15
			Applied $^{15}\text{NH}_4^+$ -N recovered, % of ^{15}N added			
Soil N	16.70	13.90	11.84	13.85	13.98	19.98
Plant N	63.10	60.35	59.63	55.50	60.54	61.55
N loss	20.20	25.75	28.53	30.65	25.48	18.47
			Applied $^{15}\text{NO}_3^-$ -N recovered, % of ^{15}N added			
Soil N	6.10	5.40	6.33	7.43	6.42	6.75
Plant N	38.10	46.65	60.50	52.15	48.18	56.03
N loss	55.80	47.95	33.17	40.42	44.40	37.22

The dissimilatory reduction of nitrate- to ammonium-nitrogen under such conditions would be limited. Very low levels of ammonium-nitrogen (0.1 to 0.66 μg ammonium-nitrogen-15/g, Table 20) converted from nitrate-nitrogen treatment in the study suggest that respiratory nitrate reduction to ammonium-nitrogen was not a significant process in the system.

The immobilization of nitrate- to organic-nitrogen, although smaller in magnitude than the denitrification losses (discussed later) is important in overland treatments such that it would reduce nitrate losses through runoff, subflow or leaching through the soil profile.

The data presented in Table 20 also indicate that the fraction of added nitrogen retained in the soil (ammonium + nitrate + organic fraction) was much greater in the ammonium-nitrogen amended treatments than in the nitrate-nitrogen amended treatments. Soil nitrogen in the ammonium-nitrogen treatments ranged from 11.84 to 22.19% of total labelled nitrogen added whereas only 5.40 to 7.16% of added nitrogen was retained in the soil in the nitrate-nitrogen treatments. Rye grass plants (shoots and roots) accumulated up to 25% more nitrogen in the ammonium-nitrogen treatments compared to nitrate-nitrogen treatments. The mass balance of nitrogen added to the soil-plant system during the 38-day experiment shows that 18.47 to 30.65% of added ammonium- and 33.17 to 55.80% of added nitrate-nitrogen were lost from the system. Denitrification reactions resulting in nitrogen and nitrous oxide gases production and ammonia volatilization may account for these nitrogen losses. However, soil pH values in the ammonium-nitrogen treatments ranged from 5.4 to 6.4, and in the nitrate-nitrogen treatments from 6.6 to 6.8. The acidic soil conditions in the ammonium-nitrogen treatments preclude the possibility of any significant ammonia volatilization occurring in the system (EPA, 1977).

Loss of applied ammonium- and nitrate-nitrogen due to denitrification reactions increased as nitrogen additions were made with time. The data plotted in Figure 15 suggested the rate of nitrogen disappearance followed a zero order reaction and was independent of ammonium- or nitrate-nitrogen concentrations. Similar results have been reported by Broadbent and Clark (1965) and Patrick (1960) who suggested that the rate of denitrification was independent of nitrate-nitrogen concentration and followed a zero-order kinetics. The slope of the nitrogen loss calculated from the linear regression analysis in the experiment demonstrates that the rate of nitrogen loss in the nitrate-nitrogen treatments was about two times the rate of ammonium-nitrogen treatments (3.9 μg nitrogen-15/g/day and 2.09 μg nitrogen-15/g/day, respectively). The complete disappearance of nitrate-nitrogen in the soil fraction in both ammonium- and nitrate-nitrogen treatments strongly suggests that

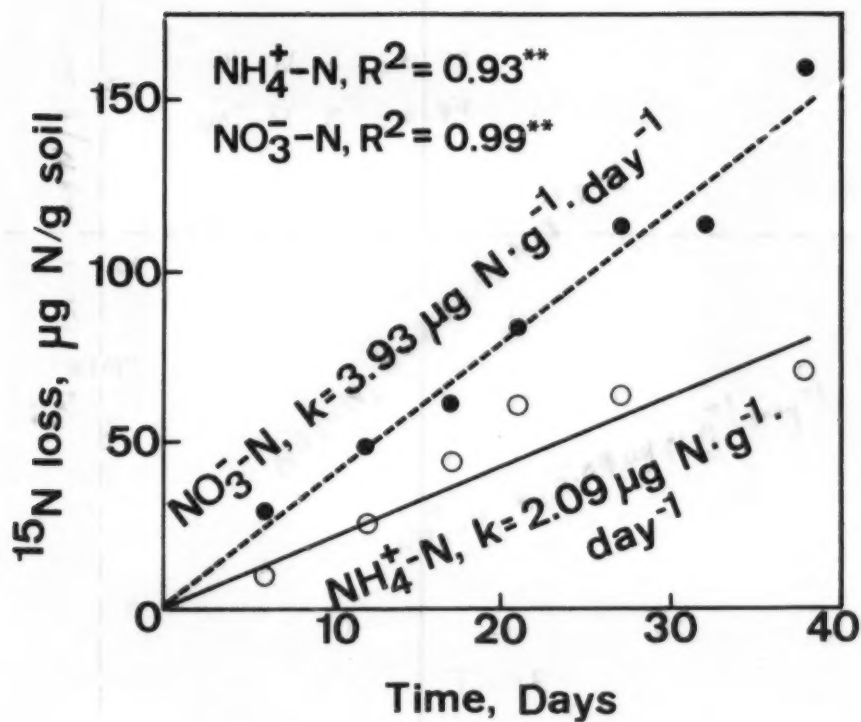
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Figure 15. Kinetics of nitrogen-15 loss in labelled ammonium- and nitrate-nitrogen treatments in Olivier soil-rye grass system.

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the denitrification process was not a limiting factor in the gaseous loss of applied nitrogen.

NITROGEN REMOVAL PROCESSES - A GENERAL DISCUSSION

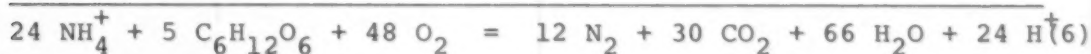
The predominant form of nitrogen in the wastewater is usually ammonium-nitrogen, although some nitrate-nitrogen in the preapplication treated secondary effluent, and small amounts of organic-nitrogen may be present (EPA, 1977; Lee and Peters, 1978; Jenkins et al., 1978). When wastewater is applied to a vegetated sloped soil at a flow rate exceeding the infiltration capacity of the soil a variety of physical, chemical and biochemical reactions are initiated. The effects of physical factors such as hydraulic characteristics of the soil, the friction slope and the slope angle which can influence the direction and intensity of ammonium-nitrogen movement in the overland flow system are discussed earlier in Section 3. The contribution of major chemical and biochemical processes significant in the renovation of wastewater were investigated in the experiments reported in this section. A schematic diagram of various nitrogen removal processes is presented in Figure 16.

Volatilization of applied ammonium-nitrogen as free ammonia from the soil surface is an important chemical reaction resulting in the loss of applied ammonium-nitrogen to the atmosphere (Ryan and Keeney, 1975). The magnitude of ammonia volatilization is largely controlled by the pH of soil and applied wastewater, loading rates, clay content of the soil, cation exchange capacity, plant canopy, the ammonium-nitrogen concentration gradient between the soil-water surface and the atmosphere, and temperature (Mills et al., 1974; Emerson et al., 1975; Fenn and Kissel, 1976; EPA, 1977; Beauchamp et al., 1978). Qualitative monitoring of ammonia volatilization in the overland flow experiment conducted in Olivier soil-Bermuda grass system (Experiment 3) and other growth chamber studies conducted in Mhoon and Grenada soils (Experiments 4 and 5) in the studies indicated that loss of ammonium-nitrogen through volatilization during overland flow treatment of municipal wastewater may be appreciable especially under alkaline soil conditions. There are no data available on the field estimates of ammonia volatilization during land application of wastewater.

Of the biochemical reactions nitrification and denitrification are very important in the removal of wastewater nitrogen. Nitrification is important because it converts ammonium-nitrogen, adsorbed on the soil exchange complex and not easily diffusible, to nitrate-nitrogen that moves readily to the lower anaerobic soil layers with the percolating water. Working with flooded Crowley soil, Reddy et al. (1976) and Patrick and Reddy (1976) determined that the rate of downward nitrate diffusion from the aerobic soil layer was over six times higher than that of

ammonium diffusion. The environmental parameters that may limit biological oxidation of ammonium- to nitrate-nitrogen include nitrifying microorganisms, soil pH, temperature, and oxygen supply. Nitrification potential which is a net effect of various factors is an important soil property determining the maximum possible loss of applied ammonium-nitrogen through denitrification reactions. Incomplete nitrification of added ammonium-nitrogen in the overland flow experiments conducted on Mhoon soil (Experiment 1) and Olivier soil (Experiment 3) and in other growth chamber studies with Grenada soil (Experiment 5) were occurring in the studies. This indicates that nitrification reaction may be limiting the proportion of nitrate-nitrogen available for denitrification reactions.

Denitrification is important because it is the principal biochemical process by means of which nitrate-nitrogen is lost from the soil system through conversion to nitrous oxide and dinitrogen gases (Keeney, 1973; Brezonik, 1977). The environmental factors important for denitrification of nitrate-nitrogen include easily available energy source, moderately reduced soil conditions, favorable soil pH and temperature and a large population of denitrifying microorganisms. Under the conditions of the overland flow experiments (Experiments 1, 2, 3, and 6) the loss of applied ammonium-nitrogen attributed to denitrification reactions ranged from 2.9 to 35.4%. In the other growth chamber studies with Olivier, Mhoon and Grenada soils (Experiments 4, 5, and 7) where alternate oxidized and reduced soil conditions were created with controlled soil moisture, loss of applied ammonium-nitrogen was as high as 59%. The results of overland flow and growth chamber experiments show that no significant accumulation of nitrate-nitrogen occurred in the soil mass which indicated that denitrification process was not a limiting factor in the gaseous loss of applied nitrogen. The overall nitrification-denitrification reaction may be written as follows:



The nitrate-nitrogen formed during these processes, therefore, is an intermediate product in the overall pathway between ammonium-and nitrogen gas (Patrick and Reddy, 1976).

The results of the studies indicate that 23 to 62% of applied nitrogen was taken up by the growing plants in the overland flow and other growth chamber studies. The plant uptake, therefore, accounted for the maximum removal of wastewater nitrogen compared to other chemical and biochemical

processes. This significantly large fraction of nitrogen removal by the plants confirms that vegetative growth may be an efficient process in the wastewater treatment in an overflow system. However, very little research has been conducted on the role of plant species in the establishment of land treatment models.

Some of the biochemical processes that have indirect influence in reducing the levels of nitrogen in the runoff and subflow include immobilization of ammonium-nitrogen by the microorganisms and soil organic matter and conversion of nitrate-nitrogen to organic-nitrogen. Conversion of both ammonium- and nitrate-nitrogen to organic nitrogen and subsequent mineralization of organic nitrogen to ammonium form further facilitates removal of nitrogen by various processes. The role of these processes in the overall distribution of nitrogen in land application of wastewater and eventual reduction of groundwater and stream contamination are illustrated in Figure 16.

CONCLUSIONS

The contribution of various biochemical transformations in the removal of wastewater nitrogen in an overland flow treatment system were investigated in the seven sets of experiments discussed earlier. The results of these studies which may be significant in the land application of municipal wastewater are summarized as follows:

1. The redox potential values of surface soil in various overland flow experiments remained well oxidized indicating the existence of favorable conditions for the nitrification of ammonium-nitrogen added to simulated wastewater. In the sub-surface soil, redox potential values ranged from well oxidized to very reduced. These aerobic-anaerobic zones in the soil mass facilitate nitrification-denitrification processes and enhance nitrogen losses to the atmosphere.
2. Low soil pH in the range of 5.1 to 6.0 and the lack of easily available energy source resulted in negligible losses of applied ammonium-nitrogen through nitrification-denitrification reactions (experiments 1 and 2). Unfavorably low pH is known to inhibit the growth of both nitrifying and denitrifying organisms resulting in reduced gaseous nitrogen loss. Absence of readily available carbon source results in reduced activity of denitrifying microorganisms.
3. The loss of ammonium-nitrogen through ammonia volatilization reaction in the overland flow experiments and sealed growth chamber studies accounted for about 5% of the total nitrogen added. The pH of soils used in various ammonia volatilization studies ranged from 6.4 to 7.6 and would therefore

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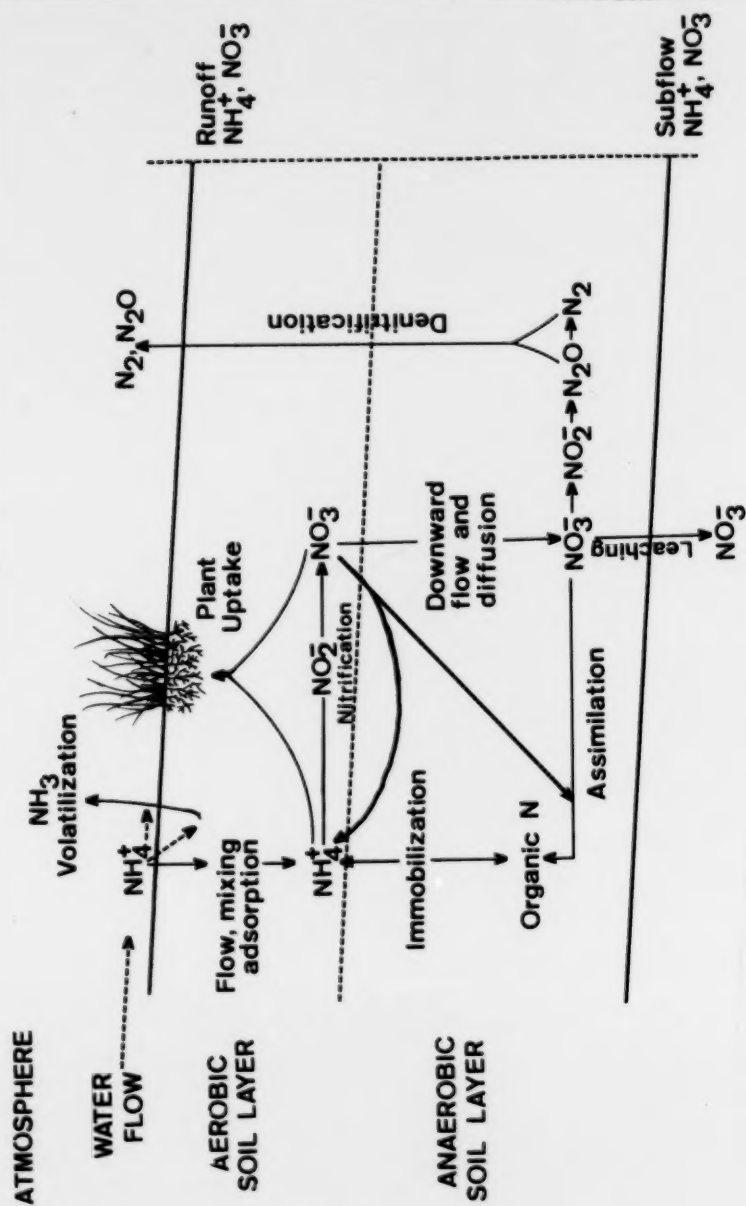


Figure 16. A schematic diagram of various nitrogen removal processes occurring in an overland flow treatment of wastewater.

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explain for the relatively small losses of applied ammonium-nitrogen through ammonia volatilization reactions. Published literature suggests that in more alkaline soil conditions ammonia volatilization losses would be appreciable.

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4. Incomplete nitrification of added ammonium-nitrogen in the overland flow experiments conducted on Mhoon and Olivier soils and in the growth chamber studies with Grenada soil simulating overland flow environment was occurring in the studies. These results suggest that nitrification reactions may be limiting the proportion of nitrate-nitrogen available for denitrification reactions.

5. The movement of ammonium-nitrogen in the simulated wastewater applied to the overland flow model was restricted to the upper end of the slope. Most of the residual ammonium-nitrogen recovered at the end of overland flow experiments was present in the top few centimeters of soil mass. More nitrate-nitrogen had moved downslope and in the subsurface soil compared to ammonium-nitrogen.

6. The loss of applied ammonium-nitrogen attributed to denitrification reactions in the overland flow experiments ranged for 2.9 to 35.4%. In the growth chamber studies where alternate oxidized and reduced soil conditions were attained with controlled soil water content, loss of applied ammonium-nitrogen was as high as 59%. No significant accumulation of nitrate-nitrogen in the soil mass indicated that denitrification process was not a limiting factor in the gaseous loss of applied nitrogen.

7. The plant uptake of nitrogen in the overland flow and growth chamber studies accounted for 23 to 62% of applied ammonium-nitrogen and thus resulted in the maximum removal of wastewater nitrogen compared to other chemical and biochemical processes. Also, preferential uptake by rye grass plants of ammonium-nitrogen over nitrate-nitrogen was demonstrated in the studies.

8. The presence of vegetative cover in the overland flow experiments significantly affected only the pool of organic-nitrogen and did not increase the loss by applied nitrogen through denitrification reactions.

9. The results of overland flow experiments and growth chamber studies demonstrated that the rate of nitrogen loss in the nitrate-nitrogen treatments was about two times the magnitude of the ammonium-nitrogen treatments. The rate of nitrogen disappearance followed a zero order reaction and was independent of ammonium- and nitrate-nitrogen concentrations. The results of the experiments suggest that the gaseous

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loss of applied nitrogen can be maximized during land application of wastewater if conditions favorable for simultaneous nitrification-denitrification reactions are attained through careful manipulation of soil-plant systems.

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SECTION 5

EFFECTS OF CHANGES IN REDOX POTENTIAL AND pH ON SOIL PHOSPHORUS
SORPTION, AND MOBILITY UNDER CONTROLLED LABORATORY CONDITIONS

INTRODUCTION

When wastewater is applied to land, either in an irrigation, infiltration-percolation, or overland flow system, increasing water saturation causes changes in the oxidation-reduction state (commonly measured as redox potential) and pH of the soil. One of the most commonly occurring and reactive cations found in soil is iron, existing as ferric-iron in normal aerated soils. As the redox potential falls, ferric-iron is increasingly reduced* to ferrous-iron, and this reduction* is accompanied by the dissolution of iron compounds particularly in acid soils (Gotoh and Patrick, 1974).

Wastewater commonly contains dissolved orthophosphate at concentrations up to 20 µg phosphorus/ml. However, when wastewater is continually applied to land the actual concentrations become much higher because of the loss of water by evapotranspiration and infiltration. Phosphate, on the other hand, tends to be immobilized in the top layers of soil by processes of adsorption, precipitation, absorption, and biological incorporation. Soils vary widely in their capacity to immobilize phosphate. Because of the predominance and rapidity of the adsorption process, the amounts of surface active soil components, such as the hydrous oxides of iron and aluminum, calcium carbonates, and layer silicate minerals, are most closely related to the immobilization capacity. However, under reduced conditions large increases in the concentration of cations such as iron could make precipitation reactions very important in phosphate immobilization.

In recent years it has become evident that the soil phosphorus immobilization or sorption capacity is possibly the most important soil criterion in the selection of sites for the land application of wastewater. The use of the Langmuir adsorption equation to determine the phosphorus retention capacity of soils

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*"reduce" and "reduction" are used in this report strictly in reference to a decrease in redox potential or oxidation state.

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was first demonstrated by Olsen and Watanabe (1957). This procedure was also proposed by Ellis (1973) to rate soils in terms of their suitability for land application of wastewater. However, Gunary (1970) pointed out that the traditional form of the Langmuir equation considerably underestimates the sorption maximum, and subsequently Holford, Wedderburn, and Mattingly (1974) used the extended two-surface form of the Langmuir equation to make a much more accurate estimate of the sorption maximum. Even this equation may underestimate the total sorption capacity because at high phosphorus concentrations precipitation may become a dominant mechanism (Holford and Mattingly, 1975a).

Although the importance of phosphate sorption capacity is self-evident, the factors controlling phosphorus mobility in soil are not so readily understood. It is generally assumed that mobility is directly related to sorption capacity so that the greater the sorption capacity the smaller will be the tendency of phosphorus to leach through the soil. This is not necessarily correct because the concentration of phosphorus in the soil solution is controlled by the buffer capacity and only partly by the sorption capacity. In soils with the same sorption capacity and the same quantity of labile solid phase phosphorus, the concentration of phosphorus in solution (and hence the mobility of phosphorus) will be inversely related to the buffer capacity (Holford and Mattingly, 1976). Hence, as phosphorus accumulates in soil during the land application of wastewater, the rate of increase in phosphorus mobility will be inversely related to the buffer capacity. In other words the amount of phosphorus which can leach through the soil per unit of phosphorus added to the soil is inversely proportional to the buffer capacity and is directly proportional to the quantity of labile phosphorus already in the soil.

The Langmuir two-surface equation is useful, not only for determining the sorption capacity, but also for estimating the buffer capacity, because the latter can be represented by the slope of the sorption isotherm. In its simplest form the Langmuir theory of adsorption is based on the existence of a finite population of adsorption sites with a specific net bonding energy. These two parameters are represented by the two Langmuir constants; these characterize the sorption process, because the product of the two constants gives the maximum buffer capacity of the system (Holford and Mattingly, 1976).

Because of their influence on the iron chemistry of the soil-water system, chemical reduction and accompanying changes in pH can have overriding effects on phosphorus sorption and mobility in soils used for wastewater application. The selection of the most suitable sites and management strategies for the land application of wastewater is dependent on an adequate

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understanding of the magnitude and nature of these effects.
Hence, the aims of this research program were:

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1. to measure the effects of controlled reduction and pH changes on phosphorus sorption and mobility in a previously aerobic soil;
2. to measure the effects of controlled re-oxidation and pH on phosphorus sorption and mobility in soils subject to varying degrees of prior anaerobiosis;
3. to elucidate the processes responsible for changes in phosphorus sorption and mobility associated with reduction and re-oxidation;
4. to study the kinetics of anaerobic changes which affect subsequent phosphorus sorption and mobility.

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MATERIALS AND METHODS

Soil

A large bulk sample of Crowley silt loam (Typic Albaqualfs) was prepared by air drying, grinding to 0.5-mm and thorough mixing. Crowley silt loam was selected because it had been commonly used in previous related studies in this laboratory (e.g. Gotoh and Patrick, 1974) and because of its very low phosphate fertility. Some relevant chemical analyses are given in Tables 3 and 21.

Controlled Redox Potential and pH Treatments

Immediately before treatment, 0.3% rice straw (ground <0.5-mm) was thoroughly mixed with the soil to increase the energy source for microorganisms involved in reduction. Suspensions of 500 g of soil in 2850 milliliters of 0.01 M calcium chloride were incubated at $30 \pm 2^\circ\text{C}$ in 3 liter reduction flasks with constant stirring. Redox potential was decreased by the constant addition of nitrogen or argon and it was controlled by the automatic addition of air when required. A total of 200 mg of dextrose was added to each reduction flask during the course of each experiment. The pH was controlled where necessary by the addition of 2 N hydrochloric acid or 2 N sodium hydroxide. The detailed procedure for controlling redox potential and pH has been described previously (Patrick, Williams, and Moraghan, 1973). The procedure used in this study differed from that in previous studies in this laboratory in that soil suspensions were not preincubated and reduced prior to the application of controlled redox potential - pH treatments.

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TABLE 21. EFFECTS OF REDUCTION ON PHOSPHORUS SORPTION AND RELATED VARIABLES

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Redox potential (mv)	-150	+65	+500	untreated
pH	6.6	5.9	5.2	5.6
Pe (μg/g)	255	18	16	34
P conc. (μg/ml)	.017	.004	.003	.007
Fe conc. (μg/ml)	.1	trace	.1	.2
Mn conc. (μg/ml)	>40	15	.4	5.3
<u>Langmuir derived parameters</u>				
Residual variance	419	53	68	68
X_m^t (μg/g)	930	394	372	417
X_m^t -Pe (μg/g)	675	376	356	383
k' (ml/μg P)	110	45	40	63
k" (ml/μg P)	.95	.14	.13	.18
MBC x 10 ² (ml/g)	459	42	35	75
EBC x 10 ⁻² (ml/g)	60	30	28	36

The duration of incubation was 25 + 3 days. The duration of the treatment was proportional to the time taken to attain the desired redox potential, this varying from four to ten days. In this way the duration of incubation at the desired redox potential was about 18 days. The time schedule for pH changes was regulated to approximate that for redox potential.

In the re-oxidation phase of each treatment air was bubbled through the reduced suspension until a redox potential of 520 + 60 mv had been reached. The duration of this re-oxidation phase was 24 + 4 days. The pH was controlled as in the reduction phase.

The detailed treatments in each experiment were as follows:

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1. Controlled redox potentials of -150, +65, +280 and +500 mv; pH monitored but uncontrolled.

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2. Controlled redox potentials of -150, +65, +280 and +500 mv in factorial combination with pH treatments of 5.0, 6.5 and 8.0.
3. Treatments in Experiments 1 and 2 were re-oxidized to 520 + 60 mv, and the pH was controlled to 5.5 in the treatments from Experiment 1 and to 5.0, 6.5 and 8.0, respectively, in Experiment 2 during the latter one-half of the re-oxidation phase.
4. Redox potential controlled at -150 mV and pH at 6.5 for 1, 6, 9, 18, 27 and 45 days; the pH was allowed to rise naturally, taking eight days, in the 18, 27 and 45 days treatments; in the six-day treatment the pH was raised to 6.5 after two days, and in the nine-day treatment after three days of natural rise. During re-oxidation the redox potential was raised to 540 $\pm$ 20 mv and the pH was controlled to 5.5.

Phosphorus Sorption Measurements

At the end of the controlled redox/pH treatments, samples of the suspension (100 ml) were removed anaerobically and were added to nitrogen-filled centrifuge bottles containing 5 ml of potassium dihydrogen phosphate solution in 0.01 M calcium chloride ranging in concentration from 0 to 465 μ g phosphorus/g soil. The approximate initial concentrations of phosphorus in solution, after dilution with the suspensions, are given in Tables C-1 to C-11. The exact ratio of dry soil to solution in each reduction flask and in each bottle was determined gravimetrically.

Isotopically - exchangeable phosphorus was determined in the zero phosphorus treatment by equilibrating the suspension with 5 ml of 0.01 M calcium chloride containing six microcurie phosphorus-32/ml. Phosphorus sorption was determined in the other eight treatments by difference between the phosphorus remaining in solution after equilibration and that originally present. In each case equilibration was carried out for 24 hours on a reciprocating shaker (200 revolutions/minute) at 30 $\pm$ 2°C. Suspensions were then centrifuged for 30 minutes at 2250 rpm and the supernatant solutions were filtered under vacuum, through 0.45 microns millipore filters into screw-top test tubes containing sufficient concentrated sulfuric acid to give a filtrate pH of 2. This kept any dissolved iron and manganese in solution, and earlier re-oxidation was prevented by avoiding any contact between the reduced suspensions and air.

Where the results indicated that a significant amount of phosphorus precipitation was occurring the following procedure was followed to measure precipitation as distinct from adsorption. A volume of 100 ml of reduced suspension were centrifuged,

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and 80 ml of the clear supernatant were removed anaerobically and were added to nitrogen-filled bottles containing 4 ml of each of phosphate solution varying in concentration as before. The previous procedure was then followed to measure phosphorus sorption which, because of the absence of any soil material, must have been caused solely by precipitation.

Chemical and Radiochemical Analyses

Phosphorus analyses were carried out immediately after filtering by the method of Truog and Meyer (1929) using a Bausch and Lomb Spectronic 21. Radioactivity was measured by Cerenkov counting using a Beckman liquid scintillation system. The isotopically-exchangeable phosphorus (P_e) was calculated from:

$$P_e = P \text{ sol}/F \quad (7)$$

where $P \text{ sol}$ = P in solution ($\mu\text{g/g}$ soil) and F = fractional activity after 24 hours exchange.

The pH of the centrifugate was measured using a Beckman meter and combination glass electrode after removing a sample for phosphorus and other analyses. The acidified filtrates were measured for iron, manganese and calcium by atomic absorption spectroscopy using a Perkin-Elmer double beam model 360 spectrophotometer. All chemical analyses were carried out in 0.01 M calcium chloride.

Calculation of Phosphorus Sorption Parameters

Unless otherwise stated all measurements of sorption included isotopically-exchangeable phosphorus (P_e).

Where the phosphorus sorption isotherms fitted the Langmuir two-surface adsorption model (Holford, Wedderburn and Mattingly, 1974) it was used for the calculation of the sorption parameters as in the following equation:

$$x = \frac{k' x_m' c}{1 + k' c} + \frac{k'' x_m'' c}{1 + k'' c} \quad (8)$$

where x = amount sorbed, x_m = maximum sorption capacity, k = sorption/desorption equilibrium constant related to the bonding energy, and c = equilibrium solution concentration. The computer program used for calculating the parameters was based on the unweighted non-linear least-squares Gauss-Newton procedure (Bard, 1970).

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The phosphorus buffer capacity of the soil system, was calculated from the slope of the sorption isotherm. The instantaneous or equilibrium buffer capacity (EBC), which is the slope of the isotherm at the measured concentration of P in solution, was calculated from:

$$dx/dc = \frac{k'x_m}{(1 + k'c)^2} + \frac{k''x_m}{(1 + k''c)^2} \quad (9)$$

The maximum buffer capacity (MBC), which is the maximum slope of the sorption isotherm as c tends to zero, was calculated from:

$$(dx/dc)_{c \rightarrow 0} = k'x'_m + k''x''_m \quad (10)$$

This is a soil characteristic controlled solely by soil properties and is independent of the quantity of labile phosphorus in the soil (Holford and Mattingly, 1976).

RESULTS AND DISCUSSION

Experiment 1. Effects of Reduction on Phosphorus Sorption by Crowley Soil Without pH Control

The major effects of various levels of chemical reduction on phosphorus sorption and related variables are shown in Table 21 and Figure 17. Slight reduction (500 mv) caused a decrease in all measured variables, while moderate reduction (65 mv) caused an increase in pH and manganese concentration but similar decreases in the other variables. The effects of slight to moderate reduction on phosphorus sorption and phosphorus buffering were negligible, and the most significant effects were on the concentration of phosphorus in solution (phosphorus concentration) and the quantity of labile phosphorus (Pe). It is possible that the decrease in phosphorus concentration and labile phosphorus were associated with the addition of glucose and the extended period of incubation. Both of these factors would allow an increase in the population and activity of microorganisms with a consequent decrease in the quantity of labile phosphorus and phosphorus concentration in solution. At the same time the reduction was not great enough to cause any significant change in the iron chemistry of the system.

Reduction to -150 mv had a dramatic effect on all the variables except iron concentration in solution. The large increase in pH, phosphorus concentration, and phosphorus sorption capacity have all been reported previously (Khalid et al., 1977)

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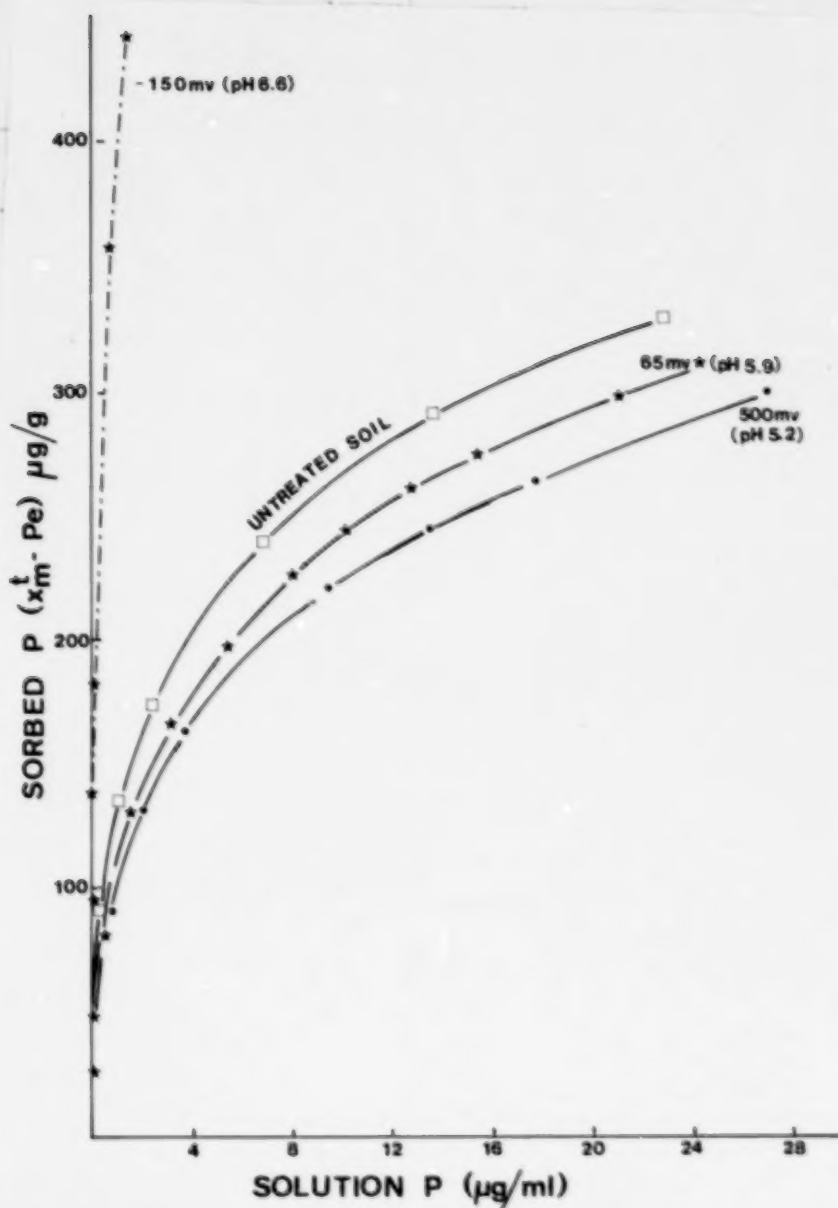


Figure 17. Effect of reduction on phosphorus sorption isotherms at equilibrium pH.

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but the very large increase in labile phosphorus has not been previously measured.

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It has been shown previously that reduction of the soil suspension causes the reduction of iron from ferric to ferrous ions, the dissolution of ferric hydrous oxides, and the consequent release of ferrous ions (Gotoh and Patrick, 1974). The simultaneous increase in pH and hydroxyl ions, which reach a maximum in about ten days, and which then appear to be buffered at about pH 6.6, probably causes the precipitation of ferrous hydroxides. These are known to be gel-like and amorphous in form (Williams et al., 1971) and consequently will sorb much more phosphorus than the original more crystalline ferric hydrous oxides such as goethite. Hence the overall effects are a large increase in phosphorus sorption and buffering capacity but no increase in solution iron concentration.

The reduction also causes the slow dissolution of ferric phosphates (Patrick, Gotoh and Williams, 1973) and the release of phosphorus adsorbed or occluded in previously precipitated ferric hydrous oxides (Chang and Jackson, 1958). Most of this dissociated phosphorus will be adsorbed on the greatly enlarged (higher x_m) and more reactive (higher k) surface of the freshly precipitated ferrous hydroxides and consequently remains in and forms the very much larger labile pool (Pe). Some of this phosphorus remains in solution, the increase in solution concentration indicating that the positive effect of the very large labile pool has been greater than the negative effect of the large increase in buffer capacity (Holford and Mattingly, 1976). This very large increase in labile phosphorus causes an increase in phosphorus mobility particularly in the short term but in the long term phosphorus mobility may decrease if labile phosphorus is retransformed into non-labile forms (see Experiment 4).

Experiment 2. Effects of Reduction on Phosphorus Sorption by Soil at Controlled pH

Sorption at pH 5.0--

Slight reduction to 500 mv had virtually no effect on phosphorus sorption characteristics and caused only a small decrease in labile phosphorus and phosphorus concentration in solution (Table 22). Increasing reduction to 65 mv caused increasing buffer capacity, increasing labile phosphorus, and increasing concentrations of iron and manganese in solution. The increase in iron concentration indicates some dissolution of iron compounds, and the release of phosphorus associated with these compounds may account for the increase in labile phosphorus at 65 mv.

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Reduction to -150 mv had the largest effect on all variables except labile phosphorus. Iron and phosphorus concentration in solution increased markedly, the sorption capacity increased, but

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TABLE 22. EFFECTS OF REDUCTION ON PHOSPHORUS SORPTION AND RELATED VARIABLES AT pH 5.0

Redox potential (mv)	-150	+65	+280	+500
pH	5.0	5.0	5.0	5.0
Pe (μg/g)	29	76	37	28
P conc. (μg/ml)	.025	.009	.006	.004
Fe conc. (μg/ml)	560	5.1	.6	.2
Mn conc. (μg/ml)	51	>50	>50	24
<u>Langmuir derived parameters</u>				
Residual variance	41	60	135	82
X_m^t (μg/g)	548	463	433	419
$X_m^t - Pe$ (μg/g)	519	387	396	391
k' (ml/μg P)	9.7	95	86	51
k'' (ml/μg P)	.05	.15	.12	.12
MBC x 10 ⁻² (ml/g)	11	152	99	57
EBC x 10 ⁻² (ml/g)	7	44	43	39

the bonding energy and consequently the buffer capacity decreased. The large decrease in buffer capacity would account for the increase in phosphorus concentration in spite of the small decrease in labile phosphorus.

The overall increase in sorption capacity obscures the fact that phosphorus sorption at low concentrations (<12 μg/ml) was lower at -150 mv than at any other redox potential (Figure 18). The shape of the sorption isotherm indicates that precipitation, as distinct from adsorption, was making a significant contribution in this particular treatment. Consequently, sorption due to precipitation alone was measured as described in the methods. This occurred in a step-wise fashion in relation to increases in phosphorus concentration (Figure 18), and the corresponding step-wise decrease in iron concentration in solution (Table C-2) supports the hypothesis that increasing ferric phosphate $[Fe_3(PO_4)_2]$ precipitation was causing the distinctive shape of

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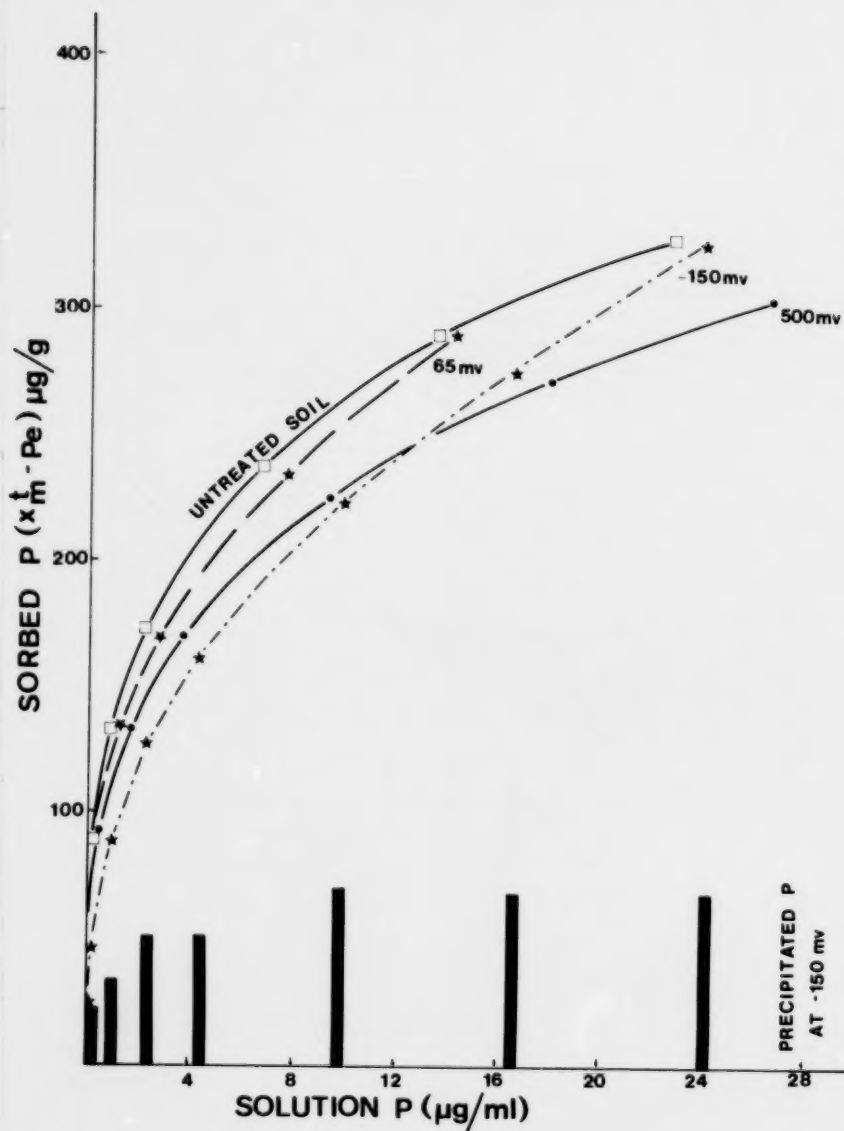


Figure 18. Effect of reduction on phosphorus sorption isotherms at pH 5.0.

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this isotherm. The lower phosphorus sorption at lower phosphorus concentrations was no doubt due to the reduction and dissolution of ferric hydrous oxides and the failure of the ferrous ions to reprecipitate as ferrous hydroxide because of the low pH. Consequently the total adsorbing surface was decreased, and the lower bonding energy indicates that the remaining composite surface had lost a component (presumably ferric hydrous oxide) with a higher bonding energy. The larger total sorption capacity was caused by the large contribution of ferric phosphate precipitation due to the high concentration of ferrous ions.

The precipitation of ferric phosphate would also account for the lack of increase of labile phosphorus at -150 mv, because as phosphorus was released by the dissolution of ferric compounds it was reprecipitated as an insoluble phosphate which would make no contribution to the labile pool.

The very large increase in phosphorus concentration indicates a corresponding increase in phosphorus mobility which was obviously related to the very low buffer capacity. The precipitation of ferric phosphate was apparently occurring at too high a concentration to have a significant effect on phosphorus buffer capacity or phosphorus mobility.

Sorption at pH 6.5--

Slight reduction to 500 mv caused a marked decrease in the quantity of labile phosphorus and in the buffer capacity, and the near neutral pH caused the precipitation of all iron and manganese from solution (Table 23). Decreasing redox potential to 65 mv had a negligible effect on labile phosphorus and sorption capacity but it caused a marked decrease in phosphorus concentration due to the increase in buffer capacity particularly at 280 mv. Manganese concentration increased to about 13 $\mu\text{g/ml}$ at -150 mv. The increase in bonding energy at +280 and +65 mv shows that there must have been some change in the surface reactivity of the iron compounds although there was no sign of any iron remaining in solution after its reduction and partial dissolution (Gotoh and Patrick, 1974).

In the most reduced treatment (-150 mv) the effects were virtually the same as in Experiment 1 where the pH was allowed to reach its natural level of 6.6. Again the residual variance between observed and predicted sorption was very high, showing that the Langmuir equation gave a poor fit to the actual isotherm points. Although the sorption capacity was no doubt greater than in Experiment 1, a ten-fold increase would be unlikely. It is noteworthy, however, that the sorption capacity, but not the buffer capacity, was greater than in any other treatment of this study (Figure 19).

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TABLE 23. EFFECTS OF REDUCTION ON PHOSPHORUS SORPTION AND RELATED VARIABLES AT pH 6.5

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Redox potential (mv)	-150	+65	+280	+500
pH	6.5	6.5	6.5	6.5
Pe (μg/g)	255	40	30	18
P conc. (μg/ml)	.017	.004	.002	.006
Fe conc. (μg/ml)	tr	0	0	0
Mn conc. (μg/ml)	36	13	tr	0

Langmuir derived parameters

Residual variance	632	139	111	34
X_m^t (μg/g)	10064	432	387	395
$X_m^t - P_e$ (μg/g)	9809	392	357	377
k' (ml/μg P)	66	94	239	26
k'' (ml/μg P)	.02	.15	.19	.12
MBC x 10 ⁻² (ml/g)	325	100	180	24
EBC x 10 ⁻² (ml/g)	74	53	82	18

The large variation between duplicate sorption measurements at -150 mv suggests that pH 6.5 must have been a critical pH for the precipitation of ferrous hydroxide [Fe(OH)₂] and the subsequent sorption of phosphorus. Wherever the iron remaining in solution after phosphorus sorption was much lower; in these cases the results were not used in the calculation of the sorption isotherm because of the probably incomplete precipitation of ferrous hydroxide.

It is possible to argue that the simultaneous removal of phosphorus and iron from solution was caused by ferric phosphate precipitation (Nriagu, 1972), rather than by ferrous hydroxide precipitation followed by phosphorus sorption. However, the fact that there was no iron left in solution in either of the zero-phosphorus treatments supports the ferrous hydroxide sorption hypothesis. There would have been insufficient

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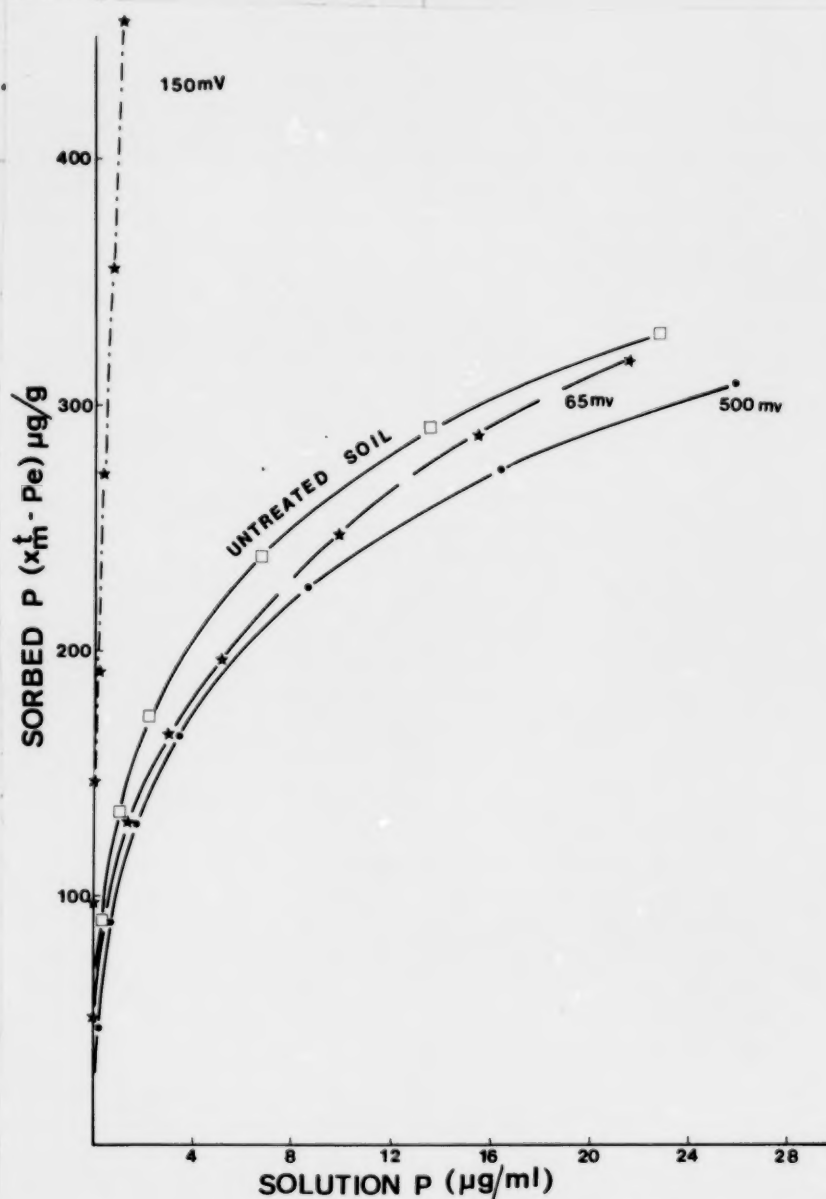


Figure 19. Effect of reduction on phosphorus sorption isotherms at pH 6.5.

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solution phosphorus in this treatment to precipitate the large amount of solution iron (at least 20 $\mu\text{g/ml}$) which would have existed at some earlier time during the reduction process (Experiment 4). At pH 6.6 (Experiment 1) there was little variation between sorption measurements, because of the more complete precipitation of the ferrous hydroxide at the slightly higher pH. In addition, precipitation of nonlabile ferric phosphate would not have caused the large increase in labile phosphorus as occurred in this treatment.

There was a marked decrease in pH during sorption at -150 mv and a smaller but significant decrease at 65 mv (Table C-3). If the reduced suspension had been supersaturated with ferrous and hydroxyl ions at the time the samples were removed for phosphorus sorption measurements, the slight change in environment may have initiated the precipitation of ferrous hydroxide. This would cause a marked decrease in hydroxyl ion concentration and the observed decrease in pH, whereas ferric phosphate precipitation would not have had this effect.

Sorption at pH 8.0--

The shapes of the sorption isotherms at pH 8.0 contrast with those at lower pH values in that there was generally less sorption in the low concentration range ($<2 \mu\text{g}$ phosphorus/ml) but more at higher concentrations. In addition there was little decrease in slope of the isotherms, and the points of each isotherm appeared to lie on at least three distinct step-wise curves (Figure 20). Consequently, it was only possible to fit a Langmuir isotherm to the first section (solution concentration $<2.3 \mu\text{g/ml}$) of each curve and this would underestimate the magnitude of the sorption capacity but not of the buffer capacity. The very low residual variance also reflects the small number of points (5 or 6) used in each calculation (Table 24).

Slight reduction caused a decrease in all measured variables except phosphorus concentration in solution. In spite of the large decrease in labile phosphorus, there was a small increase in phosphorus concentration because of the large decrease in buffer capacity. The shape of the isotherm shows that in fact there was a substantial increase in sorption capacity rather than a decrease (Figure 20). Moderate reduction caused an even greater decrease in labile phosphorus, a similar decrease in buffer capacity, but a substantial increase in sorption capacity (Table 24). In the most reduced treatment phosphorus concentration was more than doubled because of the very low buffer capacity, and the sorption capacity was only exceeded in the most reduced treatment at pH 6.5 (Table 23).

Reduction of the soil suspension at pH 8 does not appear to cause significant dissolution of iron compounds even at the lowest redox potential (Gotoh and Patrick, 1974). It is not known whether the ferric hydrous oxides were transformed to

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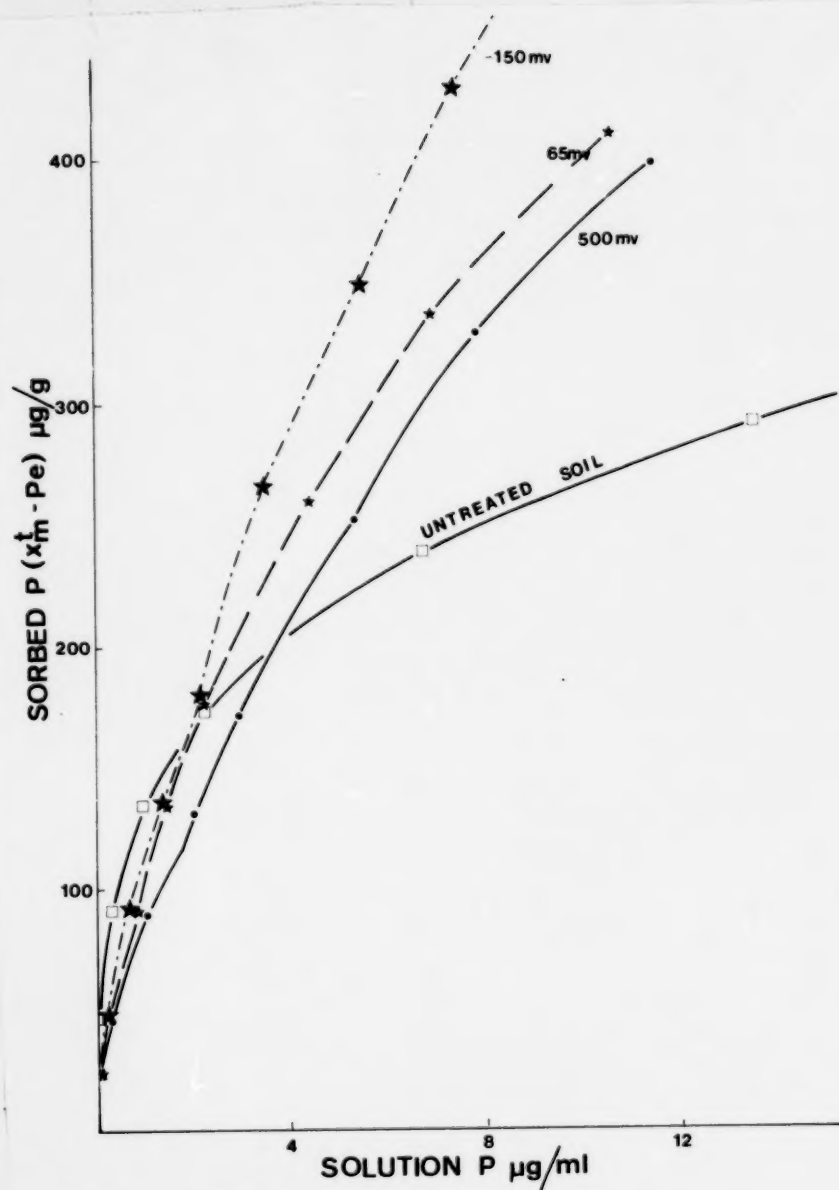


Figure 20. Effect of reduction on phosphorus sorption isotherms at pH 8.0.

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TABLE 24. EFFECTS OF REDUCTION ON PHOSPHORUS SORPTION AND RELATED VARIABLES AT pH 8.0

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Redox potential (mv)	-150	+65	+500
pH	8.0	8.0	8.0
Pe (µg/g)	17	8	12
P conc. (µg/ml)	.018	.006	.010
Ca conc. (µg/ml)	166	157	99
Fe conc. (µg/ml)	tr	tr	0
Mn conc. (µg/ml)	1.9	2.2	0

Langmuir derived parameters*

Residual variance	6	10	5
X_m^t (µg/g)	1623	795	345
X_m^t - Pe (µg/g)	1606	787	333
k' (ml/µg P)	14	41	42
k'' (ml/µg P)	.04	.11	.26
MBC x 10^{-2} (ml/g)	11	18	16
EBC x 10^{-2} (ml/g)	7	12	8

* Data calculated for low concentration range (<2-3 µg phosphorus/ml) of each isotherm.

ferrous hydroxide, but in whatever form the iron compounds existed, they would have been more negatively charged than they were in the acid treatments. This could explain the lower adsorption in the low concentration range which was associated with a smaller bonding energy particularly in the most reduced treatment. With increasing phosphorus concentration the step-wise increase in slope of the sorption isotherm, which occurred at about 2 µg phosphorus/ml and again at about 5 µg phosphorus/ml, was apparently caused by the precipitation of calcium phosphates as the high initial calcium concentration (0.01 M) at pH 8 would exceed the solubility products of both octacalcium phosphate and the dicalcium phosphate. The decreasing calcium

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concentration with increasing phosphorus sorption would also support the probability of increasing calcium phosphate precipitation (Table C-4).

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It has been shown previously that some dissolution of strengite occurs at -150 mv even at pH 8, (Patrick, Gotoh and Williams, 1973) but more complex ferric phosphates do not dissolve at pH values above 7 (Williams and Patrick, 1973). The decrease in labile phosphorus at all redox potential levels was probably caused by calcium phosphate precipitation as the phosphorus was brought into the solution phase by the decreasing bonding energy (Table 24). This may also imply that in the reduced state the phosphorus concentration in solution was being controlled by the solubility of a calcium phosphate rather than by labile phosphorus. These results indicate an overall increase in phosphorus mobility which would continue for a long period if the labile phosphorus as well as the phosphorus concentration in solution were being replenished by calcium phosphate dissolution.

Experiment 3. Effects of Re-oxidation on Phosphorus Sorption by Soil

Without pH Control During Prior Reduction--

Re-oxidation of the two higher redox potential treatments, without any further addition of glucose, allowed most of the variables to revert to what they had been in the untreated soil (Table 25). The quantity of labile phosphorus increased to its former level probably due to the release of phosphorus fixed in organic form during the earlier phase of high organic carbon additions; during the re-oxidation phase this energy source would have been exhausted with subsequent decrease in microbiological activity. The large increase in phosphorus concentration following the 65 mv treatment was apparently caused by the decrease in buffer capacity compared with the untreated soil, or the increase in labile phosphorus compared with the reduced soil.

Re-oxidation of the most reduced treatment (-150 mv) also allowed a substantial reversion of most of the variables to their former levels. Re-oxidation would cause the transformation of amorphous ferrous hydroxides to apparently more crystalline ferric hydrous oxides without a dissolution step as occurs in reduction. However, 21 days of re-oxidation were not enough to allow the ferric oxide to reach its previous state of crystallinity so that the sorption capacity remained higher than it was originally (Figure 21). On the other hand the bonding energy was much lower so that the buffer capacity was also lower. The large decrease in labile phosphorus was probably caused by the occlusion of exchangeable phosphorus during the reformation of ferric oxides. Again, this was not sufficient to bring the labile pool down to its former level of 36 $\mu\text{g/g}$ and this, together with the lower buffer capacity, allowed the

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TABLE 25. EFFECTS OF RE-OXIDATION ON PHOSPHORUS SORPTION AND RELATED VARIABLES AT pH 5.5

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Redox potential (mv)			
initial	-150	+65	+500
final	+470	+570	+570
pH			
initial	6.6	5.9	5.2
final	5.5	5.5	5.5
Pe (µg/g)	71	37	32
P conc. (µg/ml)	.020	.014	.006
Fe conc. (µg/ml)	tr	tr	.2
Mn conc. (µg/ml)	>40	.1	.1
<u>Langmuir derived parameters</u>			
Residual variance	52	42	103
X_m^t (µg/g)	507	390	378
$X_m^t - Pe$ (µg/g)	436	353	346
k' (ml/µg P)	38	40	63
k'' (ml/µg P)	.11	.11	.12
$MBC \times 10^{-2}$ (ml/g)	58	38	53
$EBC \times 10^{-2}$ (ml/g)	19	16	28

phosphorus concentrate in solution to remain high. Consequently, phosphorus mobility also remained higher than it was in the untreated soil.

With pH Control at 5.0 During Reduction and Re-oxidation--

Re-oxidation of the treatments which had undergone slight to moderate reduction caused very little change in any of the measured variables except buffer capacity (Table 26). At 65 mv,

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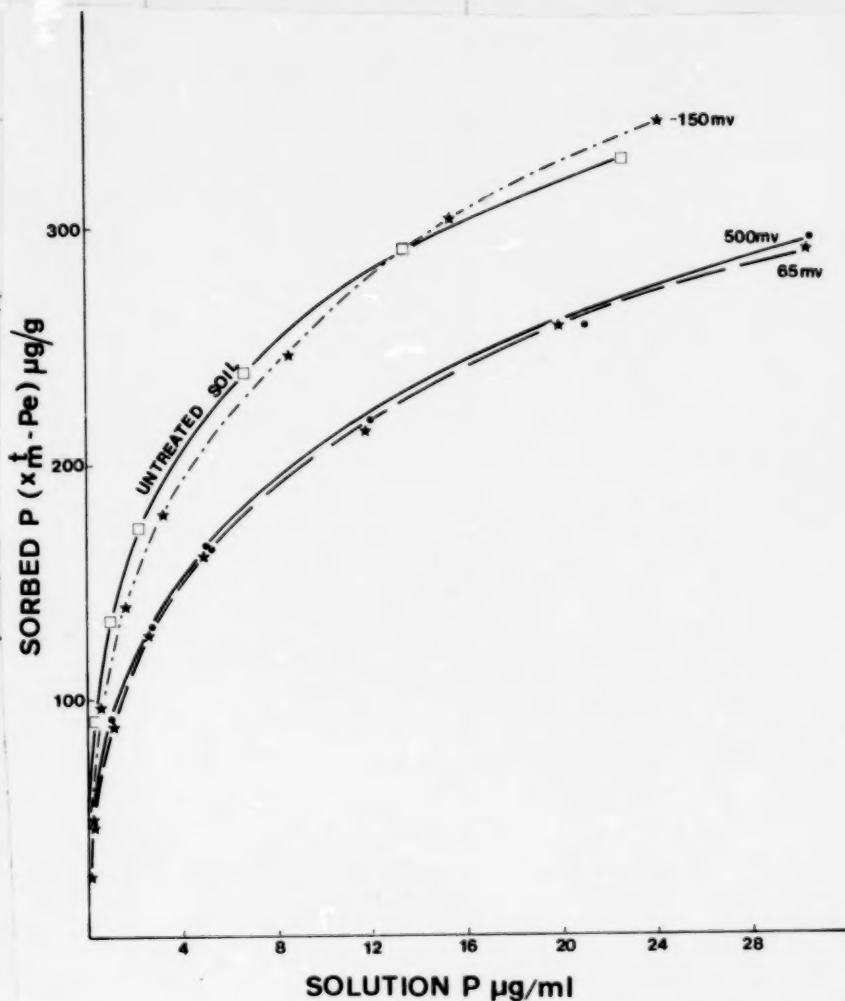


Figure 21. Phosphorus sorption isotherms after re-oxidation to 520 ± 50 mv and adjusting pH to 5.5.

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TABLE 26. EFFECTS OF RE-OXIDATION ON PHOSPHORUS SORPTION AND RELATED VARIABLES AT CONTROLLED pH*

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pH	5.0			6.5			8.0		
Redox potential (mv)									
initial	-150	65	500	-150	65	500	-150	65	500
final	500	530	560	580	580	580	500	505	515
Pe (µg/g)	250	50	50	16	16	5	13	14	21
P conc.	.014	.009	.006	.007	.008	.002	.070	.030	.040
Fe conc.	.2	tr	tr	0	0	0	0	0	0
Mn conc.	>40	29	12	.2	.1	0	0	0	0
Ca conc.	NM**	NM	NM	NM	NM	NM	78	106	81
Mg conc.	NM	NM	NM	NM	NM	NM	15	17	15
<u>Langmuir parameters</u>									
res. var.	97	113	96	33	27	19	0	1	data
X _m ^t	753	372	424	357	303	404	577	407	do not
X _m ^t - Pe	503	322	374	341	287	399	564	393	
k'	160	84	103	23	22	5.1	10	36	
k"	.97	.11	.15	.12	.10	.06	.01	.11	
MBC x 10 ⁻²	567	84	117	17	13	5	9	9	
EBC x 10 ⁻²	57	27	45	13	10	5	3	2	

* Units as in Table 21

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buffer capacity was considerably decreased by re-oxidation whereas at 500 mv it was increased. In the most reduced treatment, re-oxidation caused a very large increase in labile phosphorus and an even larger relative increase in the buffer capacity. The net effect of this was to decrease the phosphorus concentration in solution which, however, remained twice as high as that of the untreated soil. The increased buffer capacity was caused by an increase in the bonding energy as the sorption capacity ($X_m^t - Pe$) remained almost unchanged (Table 26 cf Table 22).

Re-oxidation of the most reduced treatment would cause the re-precipitation of ferric hydrous oxides from the very high concentration of ferrous in solution (Table 22) resulting in the almost complete removal of iron from solution (Table 26). These hydrous oxides would be more amorphous and more positively charged at pH 5, and consequently adsorbed more phosphorus with a higher bonding energy than the untreated soil at pH 5.6 (Figure 22). There was little change in the sorption capacity ($X_m^t - Pe$) between the reduced and re-oxidized treatment because the extra adsorption on the reprecipitated oxide surfaces would be balanced by the ferric phosphate precipitation in the reduced treatment.

The very large increase in labile phosphorus after re-oxidation of the most reduced treatment is surprising because it has been shown previously that iron phosphates and phosphorus-reactive iron oxides are more soluble under reduced than under oxidized conditions (Patrick, Gotoh, and Williams, 1973). However, the relatively high solution phosphorus concentration in spite of the very high buffer capacity (Table 26) indicates that the high labile phosphorus was a real effect. During the first ten days of re-oxidation the pH was not controlled and consequently dropped to 2.6. This may have caused the dissolution of previously inert apatite and other phosphate minerals, and the dissociated phosphorus would then enter the labile pool by adsorption onto the newly precipitated ferric oxide surfaces as the pH was raised to 5.0.

With pH Control at 6.5 During Reduction and Re-oxidation--

At pH 6.5 there was little difference in the effects of re-oxidation regardless of the degree of prior reduction. In the slightly reduced treatment sorption capacity was unchanged, but maximum buffer capacity, labile phosphorus, and phosphorus concentration in solution were as low as in any other treatment of the study. In the moderately reduced treatment labile phosphorus was decreased, but phosphorus concentration increased to that of the untreated soil because of a decrease in all sorption parameters. In the most reduced treatment there was a very large decrease in labile phosphorus, sorption capacity, and buffer capacity, and a moderate decrease in solution phosphorus (Table 26).

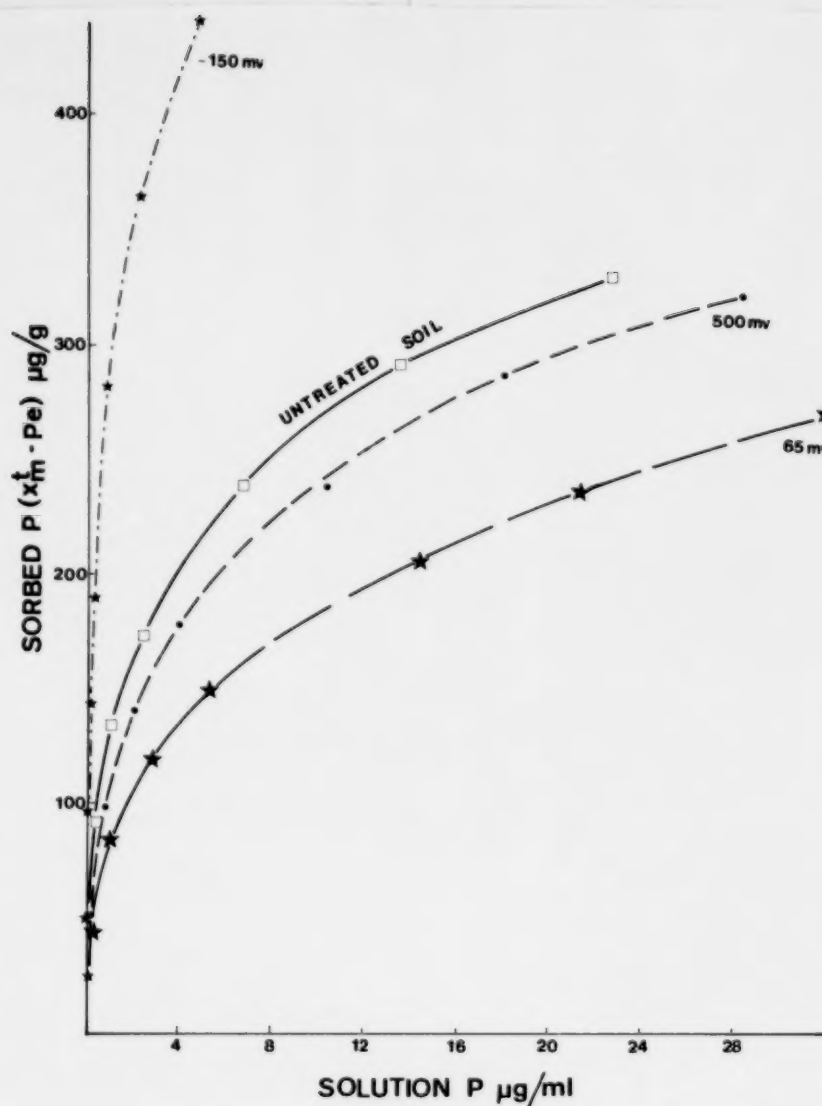
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Figure 22. Phosphorus sorption isotherms after re-oxidation to 530 ± 30 mv and maintaining pH at 5.0.

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The highly reactive amorphous ferrous hydroxide formed in the most reduced treatment would be oxidized to more crystalline ferric oxide during re-oxidation with the resultant decrease in sorption capacity (Figure 23). The longer incubation time (27 days cf 20 days), allowing more crystallinity to occur, and the decrease in surface positive charge at pH 6.5 would explain at least some of the decrease in both sorption capacity and bonding energy when compared with the effects of re-oxidation at both pH 5.5 (Table 25) and pH 5.0 (Table 26) or even the sorption parameters of the untreated soil (Table 21). It is interesting to note that the magnitude of the sorption capacity and the affinity (k') of the high energy surface were inversely related to the pH at which re-oxidation occurred. In addition, the mode of formation of the ferric oxide may be an important factor in controlling its surface reactivity because the affinity (k') of the oxide formed by the oxidation and precipitation of ferrous iron from solution at pH 5.0 was very much larger (Table 26) than that of the oxide formed by the oxidation of ferrous hydroxide precipitate at pH 5.5 (Table 25).

The mode of formation and crystallization of ferric oxides may also be involved in the loss of labile phosphorus during re-oxidation at pH 6.5. Increasing crystallization, compared with that at pH 5.5 (Table 25), may be responsible for increasing occlusion and loss of lability of phosphorus which was formerly adsorbed on ferrous hydroxide surfaces (Table 23). It is unlikely that solubility relationships of iron phosphates are involved in this loss of lability because ferric phosphates should become more soluble at increasing pH (Lindsay and Moreno, 1960) whereas in fact labile phosphorus decreased dramatically with increasing pH up to 6.5 regardless of the degree of prior reduction (Table 26).

With pH Control at 8.0 During Reduction and Re-oxidation--

Re-oxidation at pH 8.0 caused a general decrease in sorption capacity but only a very slight decrease in bonding energy (Table 26 cf Table 24). Maximum buffer capacity was halved in the moderately reduced treatment but only slightly decreased in the most reduced treatment. The Langmuir equation did not fit the data in the slightly reduced treatment so that the parameters could not be calculated (Table 26).

The most outstanding effect of re-oxidation was the very large increase in solution phosphorus in spite of relatively small changes in labile phosphorus. The fact that labile phosphorus was low (13-21 $\mu\text{g/g}$) shows that the major cause of the high phosphorus concentration in solution was the very low buffer capacity, which was generally lower than in any other treatment of this study. In the formerly most reduced treatment 3% of the total labile phosphorus existed in the solution phase at pH 8.0 whereas only 0.03% existed in the solution phase at pH 5.0.

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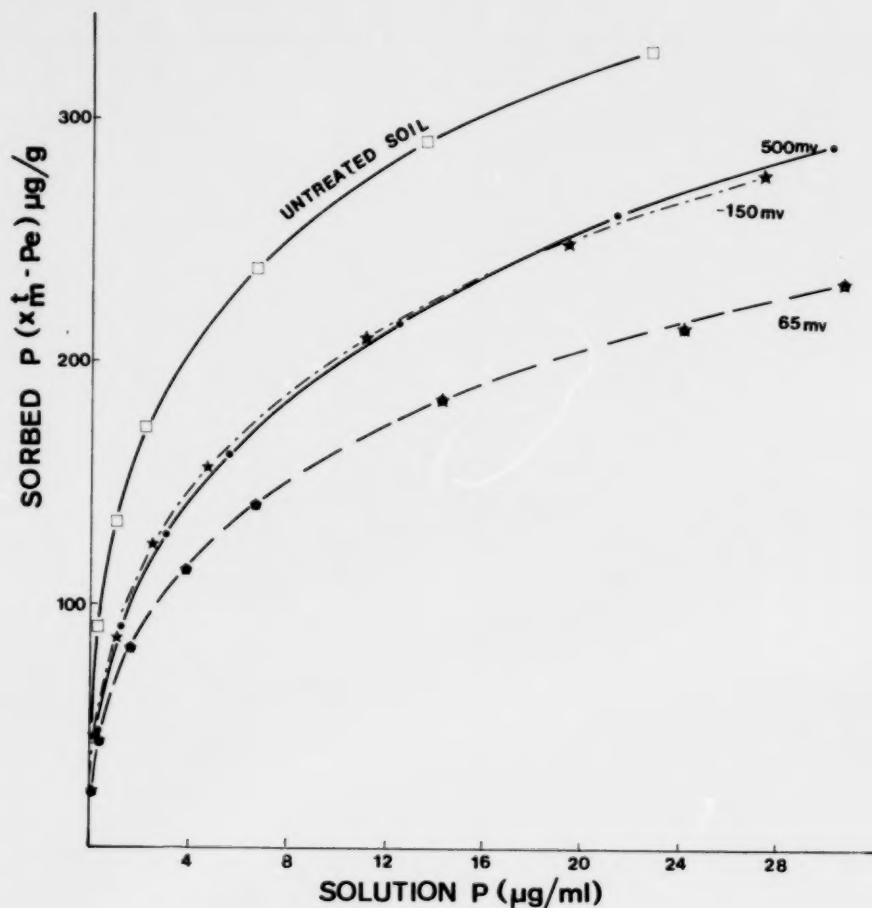


Figure 23. Phosphorus sorption isotherms after re-oxidation to 580 mv and maintaining at pH 6.5.

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The decrease in calcium concentration of the solution after re-oxidation suggests that the contribution of calcium phosphate precipitation to the total sorption capacity may have been greater than it was in the reduced state (Table C-9 cf Table C-4). Consequently, the decrease in sorption capacity was probably associated with changes in the iron compounds. It has not been established whether significant amounts of ferrous hydroxide actually existed in the most reduced treatment but it is apparent that re-oxidation caused an increase in crystallinity of the iron compounds and a resulting decrease in sorption. The magnitude of this decrease suggests that at least some of the iron compounds must have existed as the more reactive ferrous hydroxides in the most reduced treatment (Figure 24 cf Figure 20) because it is difficult to envisage any mechanism whereby the surface properties of ferric oxides could be altered to give this large change in phosphorus adsorption.

Experiment 4. Effects of Duration of Anaerobiosis on Phosphorus Sorption by Soil at pH 6.5

In the preceding experiments of this study the aim was to measure phosphorus sorption and related variables in a soil system which had reached a steady-state condition. It is known from earlier research in this laboratory that changes in the iron chemistry of soil systems subject to chemical reduction are time dependent, and it has been assumed that the iron concentration measured in the soil solution at any particular stage of reduction represents the net effect of the reduction/dissolution process and subsequent reprecipitation processes. Gotoh and Patrick (1974) fractionated the products of iron reduction into water-soluble and exchangeable iron, apparently assuming that ferrous iron in the solid phase was all exchangeable. Although it is not known how much of this exchangeable iron fraction is phosphorus reactive, it is important to know something of the kinetics of the changes induced by reduction and which will affect subsequent phosphorus sorption. These kinetics apply not only to the rate of reduction, dissolution, and subsequent reprecipitation of iron compounds which adsorb or react with phosphorus but also to the rate of reduction, dissolution, and subsequent reprecipitation of iron phosphates. With this information the most suitable management strategy can be devised for wastewater application.

Effects of Duration of Anaerobiosis--

Because of the obvious interaction between reduction and pH changes in the preceding studies, pH was maintained constant during this experiment. However, the natural pH increase was allowed to occur for at least one-third of the duration of each treatment before it was raised by alkali addition to 6.5. It was only necessary to add acid to maintain the pH at 6.5 in treatments exceeding nine days in duration.

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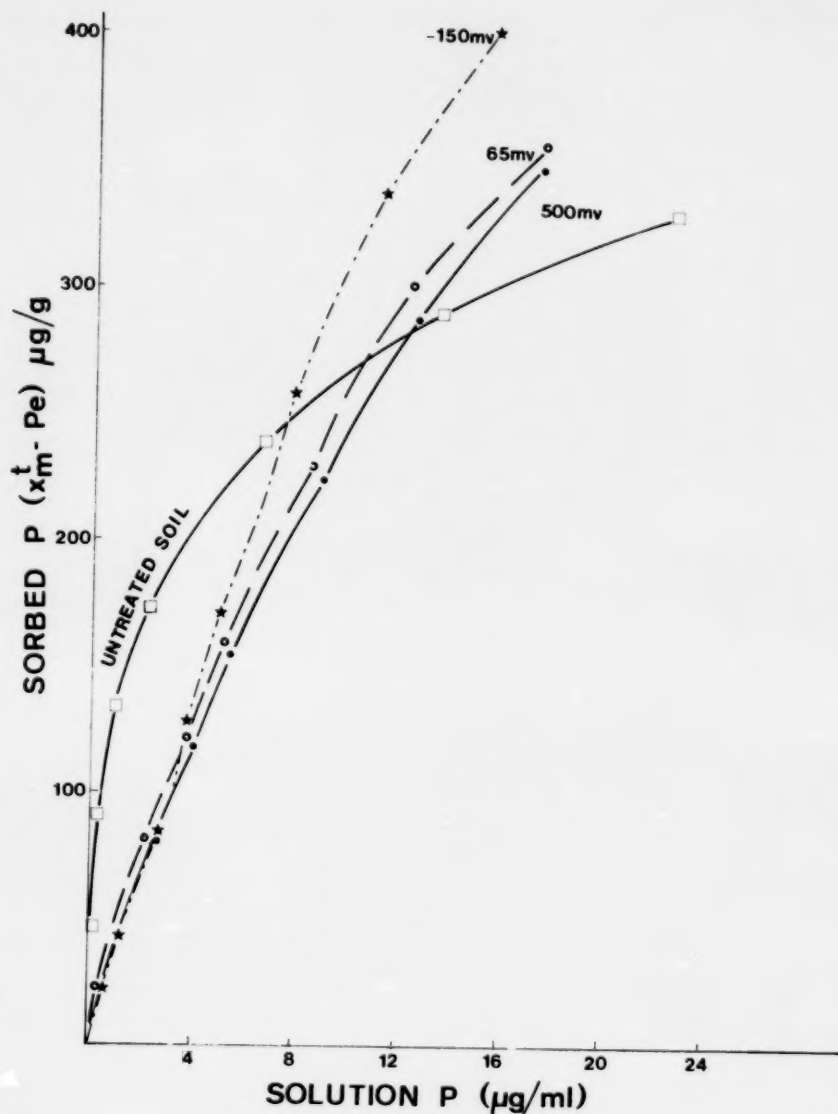


Figure 24. Phosphorus sorption isotherms after re-oxidation to 510 ± 10 mv and maintaining pH at 8.0.

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In the one-day treatment the redox potential dropped to only -90 mV. This was part of the initial very rapid reduction phase (Ponnamperuma, 1972) which was then followed in longer treatments by a temporary rising of the redox potential before it dropped more slowly to a more stable reduced condition (redox potential = -150 mv) after at least four days, depending on the rapidity with which the pH was raised. These changes are expected to be slower under natural conditions of waterlogging.

In each treatment up to 18 days, 50 mg of dextrose were added after approximately every four days, the last addition being on the penultimate day of each treatment. However, in the 27-day treatment the last addition of dextrose was made ten days before the end, and in the 45-day treatment it was made three days before the end. No dextrose was added to the one-day treatment.

The phosphorus sorption isotherms (Figure 25) show that there was a large increase in sorption after only one-day of reduction but that with increasing duration of anaerobiosis, the sorption gradually decreased until it was similar to the untreated soil at 45 days. However, at 27 days there was a large additional increase in sorption exceeding that at one day. It should be noted that each of these time treatments was carried out in a separate reduction vessel so that changes in sorption with time do not represent changes in the same flask. It is possible therefore that the large increase in phosphorus sorption at 27 days may not have occurred in the 45-day treatment.

When the Langmuir equation was fitted to the isotherm data it was found that the sorption capacity did not change significantly between one and 18 days of reduction (Table 27). The apparent change in sorption was caused by a consistent decrease in sorption energy. From the position of the isotherm the sorption energy appeared to be even lower at 45 days (Figure 25). These changes were accompanied by corresponding decreases in buffer capacity. In spite of higher sorption capacities in these shorter duration treatments the buffer capacities were lower than in the untreated soil at pH 5.6 (Table 21) but higher than in the slightly reduced soil (500 mv) at pH 6.5 (Table 23).

Surprisingly, the labile and solution phosphorus decreased with time up to 18 days (Table 27), showing that the decrease in labile phosphorus had a larger effect on solution phosphorus than the decrease in buffer capacity. The addition of dextrose shortly before measurements were made may explain the lower labile phosphorus, due to increased microbial consumption, in the 6-, 9- and 18-day treatments (Paul and DeLong, 1949), but it does not explain the apparent time effect. Apparently at some critical stage between 18 and 27 days there was a massive dissolution of phosphorus containing iron compounds followed by the precipitation

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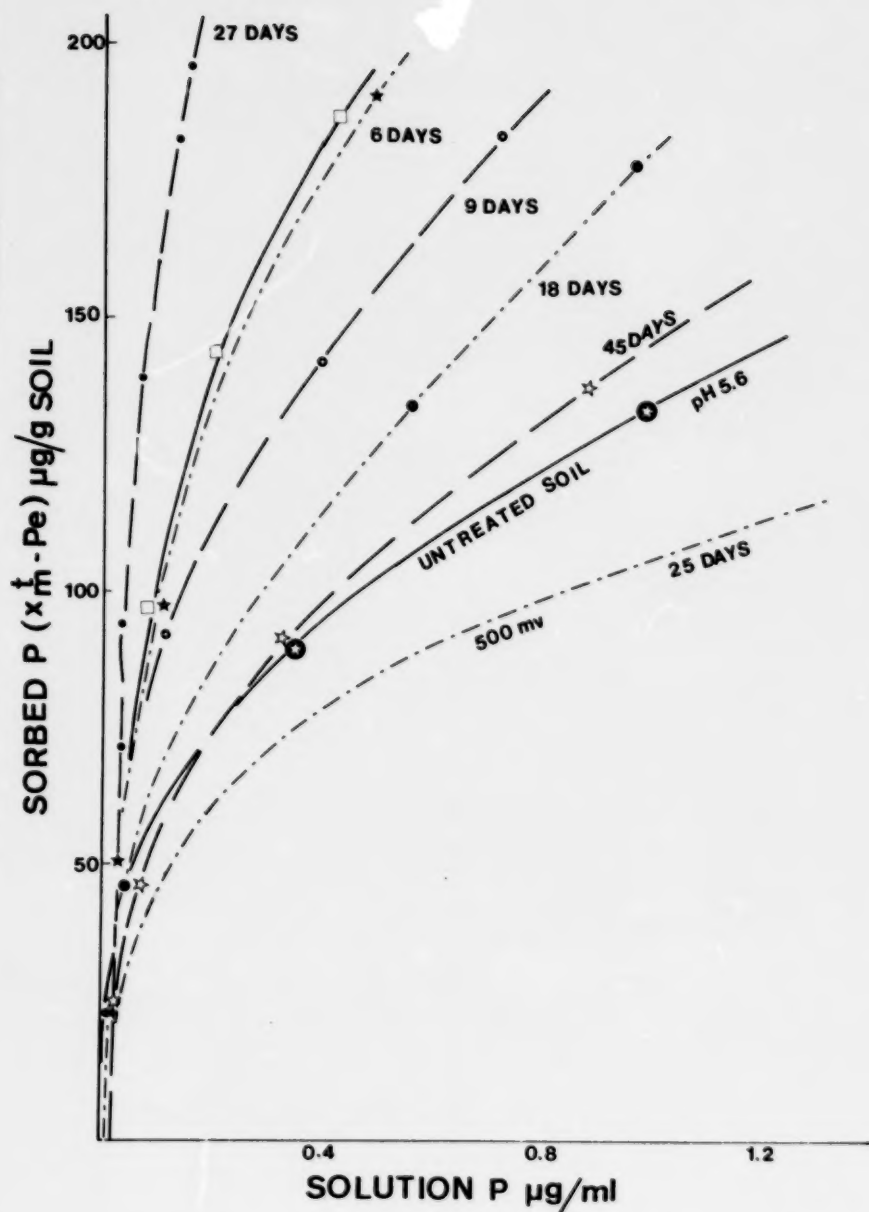


Figure 25. Effect of duration of anaerobiosis on phosphorus sorption isotherms at pH 6.5.

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TABLE 27. EFFECTS OF DURATION OF ANAEROBIOSIS ON PHOSPHATE
SORPTION AND RELATED VARIABLES AT pH 6.5

Redox potential (mv)	-90	-150	-150	-150	-150	-150
Duration (days)	1	6	9	18	27	45
Pe ($\mu\text{g P/g}$)	35	26	12	5	255	61
P conc. ($\mu\text{g/ml}$)	.004	.003	.002	.001	.017	.012
Fe conc. ($\mu\text{g/ml}$)	1.1	18	11	36	tr	37
Mn conc. ($\mu\text{g/ml}$)		22	22	NM	>40	29
<u>Langmuir derived parameters</u>						
Residual variance	75	98	59	245	419	data too
X_m^t ($\mu\text{g/g}$)	571	572	538	549	930	variable
$X_m^t - \text{Pe}$ ($\mu\text{g/g}$)	536	541	526	544	675	
k' ($\text{ml}/\mu\text{g P}$)	40	34	33	15	110	
k'' ($\text{ml}/\mu\text{g P}$)	.44	.33	.25	.14	.95	
$\text{MBC} \times 10^{-2}$ (ml/g)	65	56	43	18	459	
$\text{EBC} \times 10^{-2}$ (ml/g)	49	47	38	18	60	

of ferrous hydroxide which adsorbed the released phosphorus into a much larger labile pool and which gave a much larger sorption capacity and bonding energy. Subsequently, the ferrous hydroxide became less amorphous and more crystalline and at the same time the adsorbed phosphorus became occluded and absorbed into the aging ferrous hydroxide precipitate. The labile phosphorus therefore decreased just as it did during the oxidation of ferrous to ferric oxides (Table 25). On the other hand the higher iron concentration at 45 days shows that there was some further dissolution of iron compounds which may have led to the precipitation of iron phosphates, loss of labile phosphorus (compared with the 27-day treatment), and decrease in phosphorus buffer capacity but not necessarily sorption capacity (cf most reduced treatment at pH 5 in Table 22). The marked variability between replicates of the sorption isotherm at some phosphorus levels also suggests the possibility of phosphorus precipitation at 45 days.

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The increase in sorption capacity after only one day of reduction may have been caused by an increase in the surface area of the iron oxides due to surface coating associated with the initiation of reduction and iron oxide dissolution. With increasing reduction, the iron oxides, which would exist partly as surface coatings on other phosphorus-reactive minerals, would continue to dissolve and expose the underlying surfaces to phosphorus adsorption. Consequently, the total surface area available for adsorption (i.e. the adsorption capacity) would not necessarily decrease between one and 18 days. But if the underlying surfaces (such as layer silicate minerals) have a lower affinity for phosphorus, the net bonding energy would continue to decrease until ferrous hydroxide precipitation commenced between 18 and 27 days. At 27 days, therefore, when ferrous hydroxide would be having a major effect on phosphorus sorption, there would be a large increase in total sorption capacity as well as net bonding energy.

Effects of Duration of Prior Anaerobiosis and Subsequent Re-oxidation on Phosphate Sorption at pH 5.5--

Regardless of the duration of prior anaerobiosis, re-oxidation caused an overall decrease in sorption capacity (Figure 26) particularly in the one- and six-day treatments, and in sorption energy in the longer treatments (Table 28). However, there was a substantial increase in bonding energy, and consequently maximum buffer capacity, in the one- and six-day treatments. The sorption characteristics of the two latter treatments approximated those of the untreated soil (Table 21).

Labile and solution phosphorus more than doubled in the two short duration treatments but remained fairly constant in the nine- and 18-day treatments during re-oxidation. As noted previously, labile phosphorus decreased to 71 $\mu\text{g/g}$ in the 27-day treatment but solution phosphorus increased slightly because of the large decrease in buffer capacity. No explanation can be offered for the very low labile and solution phosphorus in the nine- and 18-day treatments either in the reduced state (Table 27) or in the re-oxidized state (Table 28). However, it is difficult to measure labile phosphorus by isotopic exchange in a system at disequilibrium as the use of the isotopic exchange equation is based on assumed equilibrium conditions. Consequently, the labile phosphorus data, particularly in the reduced treatments (Table 27), should be regarded with caution.

GENERAL DISCUSSION

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In an equilibrium soil, inorganic phosphorus exists in only three dominant phases: the solution, the adsorbed phase, and the stable mineral phase. When soluble phosphorus is added to this system in sufficient quantity (e.g. as solid fertilizer), a fourth phase occurs - a metastable mineral phase, and this

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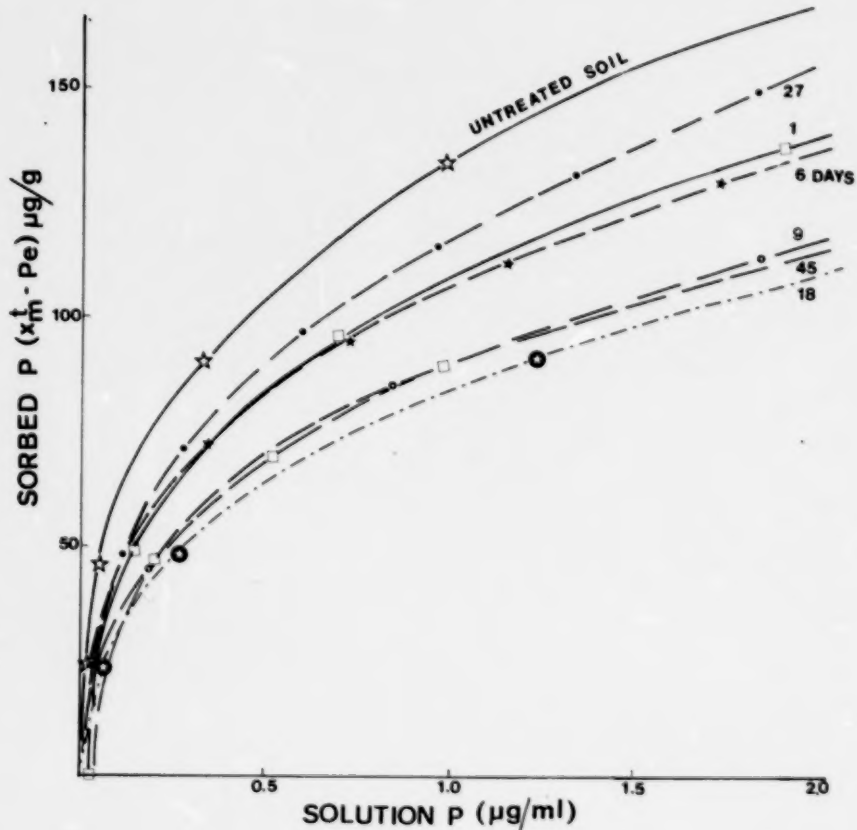


Figure 26. Effect of duration of prior anaerobiosis and subsequent oxidation at pH 5.5 on phosphorus sorption isotherms.

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TABLE 28. EFFECTS OF DURATION OF PRIOR ANAEROBIOSIS ON PHOSPHORUS SORPTION AND RELATED VARIABLES AFTER RE-OXIDATION AT pH 5.5

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Redox potential (mv)					
Anaerobic	-90	-150	-150	-150	-150
Aerobic	530	490	525	500	460
Duration (days)	1	6	9	18	27
Pe ($\mu\text{g P/g}$)	72	56	11	10	71
P conc. ($\mu\text{g/ml}$)	.011	.008	.003	.003	.020
Fe conc. ($\mu\text{g/ml}$)	0.1	0	0.1	0	0
Mn conc. ($\mu\text{g/ml}$)	23	0.2	0.3	0.6	>40
Langmuir derived parameters					
Residual variance	70	144	64	32	52
X_m^t ($\mu\text{g/g}$) $1/8''$	466	447	457	439	507
$X_m^t - P_e$ ($\mu\text{g/g}$)	394	391	446	429	436
k' (ml/ $\mu\text{g P}$)	87	91	5.2	7.2	38
k'' (ml/ $\mu\text{g P}$)	.14	.12	.04	.05	.11
$MBC \times 10^{-2}$ (ml/g)	117	110	5	7	58
$EBC \times 10^{-2}$ (ml/g)	31	37	5	6	19

follows an immediate or very rapid increase in the solution and adsorbed phases. However, the addition of wastewater, containing less than 20 μg phosphorus/ml, would not be expected to cause the precipitation of metastable mineral phosphorus unless the concentration of cations such as iron, aluminum and calcium was much greater than that usually found in soils. In most soils the dominant sorption mechanism is adsorption, and the relationship between the quantity of adsorbed phosphorus and the concentration of phosphorus in the soil solution, as defined by the adsorption isotherm, is termed the buffer capacity. The characterization of phosphorus in soil, therefore, may be defined both quantitatively and qualitatively by three fundamental parameters: the quantity

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of adsorbed phosphorus, the concentration of solution phosphorus, and the phosphorus buffer capacity. The phosphorus buffer capacity, as described in the Introduction, may be characterized by the Langmuir adsorption parameters: namely, the adsorption capacity, and the adsorption energy (Holford and Mattingly, 1976). The foregoing conceptual framework has been used in this study to interpret the effects of changes in redox potential and pH on soil phosphorus sorption and mobility.

The results have shown that there is a strong interaction between changes in redox potential and changes in pH. Decreasing redox potential causes the reduction and dissolution of ferric compounds (Ponnamperuma, 1972). It would appear that ferric hydrous oxides, existing as surface coatings on other phosphorus reactive minerals, are the first ferric compounds to dissolve, and consequently the iron concentration in solution increases but there is no increase in labile phosphorus. Eventually, ferric oxides containing occluded phosphorus, as well as ferric phosphates, dissolve releasing a large quantity of previously non-labile phosphorus.

At pH 5.0, ferrous hydroxide failed to precipitate allowing a large accumulation of ferrous iron in solution. Consequently, the solubility product of ferric phosphate was probably exceeded (Langmuir and Whitmore, 1971) and the phosphorus released by reduction was reprecipitated; hence, there was no increase in labile phosphorus when measured at 28 days. However, the dissolution of ferric oxides, leaving a residue of phosphorus reactive surfaces with lower bonding energy, caused a decrease in phosphorus buffer capacity resulting in an increase in phosphorus concentration in solution. On the other hand, the phosphorus solution capacity was increased by ferric phosphate precipitation. The precipitation of vivianite [$(\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O})$] as a fertilizer residue in waterlogged soil, has been previously reported by Lehr et al. (1959).

At the near neutral pH of 6.5 or 6.6, ferrous hydroxide apparently precipitated causing a loss of ferrous and hydroxyl ions from solution and a very large increase in phosphorus sorption and buffer capacity. However, the released phosphorus, instead of being precipitated by ferrous iron as it was at pH 5.0, was adsorbed by the very large surface of amorphous ferrous hydroxide and consequently remained in the labile pool, causing a smaller increase in solution phosphorus than at pH 5.0, because of the very large increase in buffer capacity.

The role of amorphous ferrous hydroxide in causing increase phosphorus sorption in reduced soils has been previously postulated by Williams et al. (1971) and Patrick and Khalid (1974), and the results of this study support their hypothesis. However, Patrick and Khalid's contention that phosphorus sorption was smaller in reduced soils at low phosphorus concentrations than

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in oxidized soils overlooks the fact that in the reduced soil there was a very large increase in the native adsorbed phosphorus. If this is added to their measured phosphorus sorption it would be apparent that there was much more phosphorus sorption in the reduced soil over the full range of phosphorus concentrations in solution (Tables C-1 and C-3). In other words the apparent cross-over point in their sorption isotherms for reduced and oxidized soils would not exist if the native adsorbed phosphorus was taken into account. Their other hypothesis, concerning the greater release of phosphorus in reduced soils because of a lower bonding energy of the ferrous hydroxide for phosphorus (Patrick and Khalid, 1974), is also not supported by the results of this study. The bonding energy of the reduced soils containing ferrous hydroxide actually tended to be higher ($k' = 66$ at pH 6.5 and 110 at pH 6.6) than in the oxidized soil containing ferric oxide ($k' = 63$). The higher solution phosphorus concentration in the reduced soil at pH 6.5 reflects not an increase in the release of phosphorus from the ferrous hydroxide surface or from a more soluble amorphous ferric phosphate (Patrick, Gotoh and Williams, 1973) but simply a much larger labile pool of phosphorus which maintains a higher concentration of phosphorus in solution.

The significance of a high calcium concentration, similar to that existing in wastewater, became apparent at pH 8.0 where calcium phosphates are relatively insoluble. Consequently, phosphorus sorption capacity was greatly increased due to calcium phosphate precipitation regardless of any change in the iron chemistry of the system. It is known that iron hydrous oxides retain their phosphorus affinity in alkaline calcareous soils (Cole and Olsen, 1959) but the results of the researchers indicate that increasing pH decreases the bonding energy for phosphorus probably because of the increasing negative charge of the oxide/hydroxide surfaces. This supports earlier work of Holford and Mattingly (1975b) showing a negative correlation between bonding energy and pH. It is not known whether any dissolution of iron compounds or release of phosphorus occurred at pH 8.0 as there was a decrease in labile phosphorus, but the increase in solution phosphorus was obviously associated with the decreased phosphorus bonding energy. Thus at the two extremes of pH, the suggestion of Patrick and Khalid (1974) that increased release of phosphorus in a reduced soil was caused by a decreased bonding energy, is probably correct, but this did not apply at the near neutral condition which existed in their experiments. At pH 5.0 the lower bonding energy in the reduced soil was due to the dissolution of iron oxides leaving a residue of less reactive adsorbing minerals, whereas at pH 8.0 the lower bonding energy was probably due to the higher negative charge of the iron oxide/hydroxide surfaces.

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It would seem from the results of Khalid et al. (1977) that ferrous hydroxide may have failed to precipitate in reduced soils whose pH was less than 6.2 because the apparent phosphorus sorption did not increase in reduced soils at these lower pH levels. The very steep to perpendicular isotherm of their reduced Sharkey clay indicates that phosphorus sorption at increasing concentrations of phosphorus was due to increasing precipitation of ferric phosphate in addition to adsorption on ferrous hydroxide surfaces; this soil contained very large quantities of oxalate extractable iron and soluble phosphorus.

Although there are a number of studies comparing phosphorus sorption by aerated and reduced soils, there is little information on the effects of reoxidation of reduced soils on phosphorus sorption and mobility. It has been generally observed that drying a soil after flooding decreases the mobility of phosphorus (Paul and DeLong, 1949) and that previously flooded rice-growing soils require more phosphorus fertilizer for upland crops than the same soil that has not been flooded (Willett et al., 1978). This phenomenon has been attributed to the increased reactivity of the ferric oxide in the soil, leading to an increase in the phosphorus sorption capacity and a decrease in mobility (Patrick and Mahapatra, 1968). However, the results of the present study show that re-oxidation per se does not cause an increase in sorption capacity or buffer capacity as compared with the untreated soil unless the pH is decreased to an unnaturally low level. With increasing time, beyond the 21 or 27 days of this study, the sorption and buffer capacity would be expected to decrease even further as the reformed ferric oxides become more crystalline. The results do indicate that labile phosphorus decreases, particularly at pH 6.5, apparently due to the occlusion of adsorbed phosphorus by the reformation of more crystalline ferric oxides. The longer duration and soil dehydration associated with studies on rice-growing soils may explain the differences in the present results which apply to soil suspensions re-oxidized for less than 28 days.

In this study the value of the Langmuir two-surface adsorption equation (Holford et al., 1974) for understanding the behavior of soluble phosphorus added to soil has been demonstrated. This research technique is not only useful for determining the phosphorus sorption capacity and mobility in the soil, but the shape of the sorption isotherm can be used to interpret the type of mechanism involved in sorption. It is suggested that this approach yields more information in understanding phosphorus behavior in soil than other methods of measuring phosphorus sorption which give no or inaccurate information on phosphorus bonding energy.

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CONCLUSIONS RELATED TO THE LAND TREATMENT OF WASTEWATER

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The results of this study can be applied, strictly, only to acid soils containing significant quantities (more than 1000 ppm) of reducible or oxalate-extractable iron (Khalid et al., 1977). The results for the pH 8 treatment may be applied, with modification to alkaline soils, taking into account the fact that reduction of an alkaline soil will cause a decrease in pH (Ponnamperuma, 1972) whereas these results are for an acid soil whose pH has been raised artificially to 8.0. The results of this study may be interpreted to draw the following conclusions:

1. At least three days of flooding are probably required before significant reduction and changes in phosphorus sorption and mobility occur.

Applicable to Acid Soils

2. For about 18 days after reduction has occurred, phosphorus sorption capacity will be significantly higher and phosphorus mobility will be lower than in an aerated soil.
3. After about 20 days of continuous flooding there will be a very large increase in sorption capacity and decrease in leaching losses from wastewater additions containing more than 5 µg phosphorus/ml. However, from more dilute wastewater there may be a slight increase in leaching losses compared with those from aerated soil.
4. Longer periods of flooding (more than 40 days) will cause a gradual decrease in phosphorus sorption capacity and a corresponding increase in phosphorus mobility and leaching losses.
5. Re-oxidation for periods up to 30 days will cause a marked decrease in phosphorus sorption capacity, and leaching losses from previously applied wastewater will be moderately greater than from wastewater applied to aerated soil.

Applicable to Non-Acid Soils

6. Phosphorus sorption capacity will be increased immediately by the addition of calcium in the wastewater, causing an increase in calcium phosphate precipitation.
7. With increasing reduction, pH will fall to near neutral causing a decrease in the negative charge of the iron oxide surfaces and an increase in the solubility of calcium phosphates. Consequently, phosphorus sorption by calcium phosphate precipitation will decrease but the bonding energy of the iron oxide surfaces will increase. The net effect of

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these changes would be some increase in sorption capacity and a larger increase in buffer capacity so that leaching losses would be smaller than from an aerated soil.

8. Re-oxidation would reverse the changes in pH and buffer capacity so that the phosphorus sorption capacity and leaching losses would be similar to those of an aerated soil.

Requirements for Further Research

9. Because of the importance of soil pH and reducible iron content, further research of this type needs to be carried out on a range of soils varying in pH and reducible iron content.
10. Short term kinetic studies of phosphorus sorption are important because adsorption and precipitation are fast reactions. However, the kinetics of anaerobic changes, such as pH and iron chemistry, which affect subsequent phosphorus sorption and mobility, require further study. Long term kinetic studies of phosphorus sorption due to occlusion in hydrous oxide crystals and organic incorporation also require further research.
11. Experimental evidence suggests that re-oxidation of soils can reverse the beneficial effects of reduction on phosphorus sorption capacity and mobility. Further longer term studies are required to optimize management strategies for the duration of wastewater application and re-aeration intervals.

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SECTION 6

PHOSPHORUS REMOVAL PROCESSES IN AN OVERLAND FLOW
TREATMENT OF SIMULATED WASTEWATER

INTRODUCTION

Phosphorus removal efficiency of overland flow treatment of municipal wastewater generally ranges from 40 to 80% in warm weather declining to lower levels in winter months (Thomas et al., 1976; Lee and Peters, 1978; Peters and Lee, 1978; Jenkins and Martel, 1978). Scot and Fulton (1978) reported little removal of phosphorus from municipal wastewater in cooler months in an overland flow facility in operation for over 50 years. The limited removal of phosphorus may be the result of little contact of wastewater flowing over the sloped surface with soil particles during application periods and low phosphorus retention capacities of the soils.

Phosphorus in soils is immobilized by adsorption and chemical precipitation. Precipitation involves transformation of soluble phosphates to relatively insoluble iron, aluminum and calcium phosphates which govern the phosphorus concentration in soil solution. Redox potential and pH significantly affect the solubility of these compounds in soils and thus affect phosphorus sorption. Overland flow treatment of wastewater brings changes in pH and oxidation-reduction status of soils and thus may alter the phosphorus removal efficiency of the soil mass. The effects of changes in redox potential and pH on soil phosphorus sorption and mobility under controlled laboratory conditions have been discussed in Section 5. The objectives of this research was to determine the effects of prereduced soil conditions and pH amendment on the efficiency of soil-plant system in the removal of applied phosphorus in an overland flow model established with Crowley soil.

MATERIALS AND METHODS

Crowley silt loam soil collected from Rice Experiment Station, Crowley, Louisiana and used in the phosphorus sorption studies described in Section 5 was used in this overland flow experiment. Soil characteristics of Crowley silt loam were described in Table 3. The effect of soil pretreatments on the

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removal of applied phosphorus under simulated overland flow conditions was studied in two phases:

(1) A small scale overland flow model was used to study the effects various soil pretreatments on the removal of phosphorus-32 applied to Crowley soil-rye grass system; and

(2) Phosphorus sorption and desorption characteristics of pretreated soils were studied in the laboratory using phosphorus sorption isotherms.

Overland Flow Study

The following treatments were studied in this overland flow experiment: (1) Untreated soil. (2) Prereduced soil. (3) Soil limed with 60 milliequivalents CaCO_3 /100 g of soil to raise pH to ≈ 7.5 .

Overland flow test containers were constructed of 0.63-cm thickness of plexiglas measuring 8-cm in width, 11-cm in depth and 100-cm in length (set-up similar to that illustrated in Figure 1). Air dried soil (equivalent to 8.88 kg oven-dried soil) was uniformly packed in the test containers to a depth of 8 cm and the test containers were placed on a large table in a room fitted with lights for normal plant growth. A total of six test models were prepared with two replications for each treatment.

Treatments 1 and 3 were maintained at 30 to 35% moisture while treatment 2 was flooded with about 2 cm of water constantly standing on the soil surface and the treatments were equilibrated for eight weeks. The flooded treatment, referred to as "pre-reduced" in the report, was drained to about 0.5 cm of standing water at the end of eight weeks. Rye grass seeds were sprinkled uniformly on the soil surface at the rate of 10 g/test container. The soil in the test containers for Treatments 1 and 3 were kept saturated with water for five weeks when the plants were growing while Treatment 2 had 0.5 cm of standing water. A 14-hour light period and 10-hour dark period was provided for plant growth.

The test containers were placed on 1.2% slope and one liter of tap water was applied to each test model at the rate of 10 hours per day for five days to establish overland flow pattern prior to phosphorus-32 applications. The plants were cut to a height of six centimeters and no water was applied for three days before simulated wastewater containing radioactive phosphorus was applied.

Platinum electrodes were installed at 0.5-cm, 3-cm, and 6-cm soil depths, in duplicate, in one replication only for monitoring redox potentials during overland applications. The

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maximum and minimum temperature in the overland area were recorded regularly during the length of experiment.

Phosphorus Application--

Simulated wastewater containing 20 µg phosphorus/ml as potassium phosphate (KH_2PO_4) and tagged with 0.1578 microcuries phosphorus-32/ml was applied to soil-plant system established on 1.2% slope at the rate of 1 liter/10 hour/day (equivalent to 1.25-cm water/day). Influent applications were made five days per week for four weeks. The combined runoff plus subflow from each treatment was filtered through 0.45-micron filter and the activity of phosphorus-32 in the filtrate was measured by the liquid scintillation system.

A blanket application of nitrogen and micronutrients was made to the soil-plant system after the rye grass seeds germinated, and with the first and the eleventh influent applications to attain a good plant growth.

Plant and Soil Analysis--

At the end of the four-week overland flow experiment, plants were harvested in 0- to 25-cm, 25- to 50-cm, 50- to 75-cm, and 75- to 100-cm sections downslope, were washed in distilled water and were dried at 15°C in the draft oven. Plant samples were digested in nitric acid, sulfuric acid and perchloric acid mixture (4:1:1) and were counted for phosphorus-32 activity using the liquid scintillation system.

Soil mass was separated into 0- to 25-cm, 25- to 50-cm, 50- to 75-cm, and 75- to 100-cm sections downslope. Each section was separated into 0- to 2-cm, 2- to 4-cm, and 4- to 8-cm depths. Soil samples were shaken with 0.01 M calcium chloride for one hour at a soil-solution ratio of 1:5, were centrifuged and the supernatant was counted for phosphorus-32 activity. The residual soil material from the calcium chloride extraction was shaken for 24 hours with 0.5 M sodium bicarbonate adjusted to pH 8.5 at a soil-solution ratio of 1:10. The suspension was centrifuged and the supernatant was counted for phosphorus-32 activity. Total phosphorus-32 retained by the soil complex at the end of 20 influent applications was determined by digesting the soil material as described for plant samples. The pH values of calcium chloride extracts were determined using a combination glass electrode. Soil extractions and analyses were conducted on duplicate samples.

Phosphorus Sorption Study

The phosphorus sorption and desorption behavior of pre-treated soils used in the overland flow experiment described above was studied under laboratory conditions. A 600-g sample of Crowley soil, with and without lime treatment, was transferred to glass beakers and equilibrated for 13 weeks as follows:

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Treatment 1 (Untreated)--

Unlimed soil was maintained at 30 to 35% moisture level for eight weeks followed by five weeks of equilibration at saturated soil moisture level.

Treatment 2 (Prereduced)--

Unlimed Crowley soil was equilibrated for eight weeks with 2 cm of water standing on the soil surface, followed by about 0.5 cm of water standing on the soil surface for the next five weeks.

Treatment 3 (Limed)--

Crowley soil limed with 60 milliequivalents of calcium carbonate/100 g of soil was maintained at 30 to 35% moisture level for eight weeks followed by five weeks of equilibration at saturated soil moisture level.

At the end of 13 weeks of equilibration at different soil moisture levels the incubated soils were vacuum-dried under high vacuum to avoid oxidation of any reduced iron that may have been present in the soil. Soil samples from the three pretreatments were then ground to pass through a 20-mesh sieve for determining phosphorus sorption isotherms as follows:

Soil samples, equivalent to 10 g of oven-dried soil, were shaken for 24 hours with potassium phosphate ranging in concentration from 0 to 500 μ g phosphorus/g soil in a soil-0.01 M calcium chloride ratio of 1:5. After 24 hours of equilibration, soil suspensions were centrifuged and filtered through a 0.45 μ filter. The filtrate was analyzed for phosphorus and phosphorus sorption was measured by the difference between the concentration of phosphorus remaining in solution and that added.

The fraction of freshly adsorbed phosphorus desorbed was determined by shaking the residual soil material with 0.01 M calcium chloride for one hour at a soil-solution ratio of 1:5. The soil suspension was centrifuged, filtered, and analyzed for phosphorus as above. The desorption step was repeated one more time.

The isotopically exchangeable phosphorus in the pretreated soil treatments was determined with carrier-free phosphorus-32 as described in Section 5.

Nine-point sorption isotherms were plotted and various sorption parameters were calculated from the Langmuir two-surface equation as described in Section 5.

The calcium chloride filtrates from the zero phosphorus treatments were analyzed for iron. Soil pH of all the filtrates

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was determined. The phosphorus sorption-desorption study was conducted on duplicate samples.

RESULTS

Redox Potential Measurements During Overland Flow Treatment

The redox potentials were measured at 0.5-cm, 3-cm, and 6-cm depths to determine the oxidation-reduction status of surface and subsurface soil layers. The redox potential data recorded for various treatments during the course of the experiment are recorded in Table D-1. The data for 0.5-cm and 3-cm depths are plotted in Figure 27. The redox potential values of the surface layer for various treatments fluctuated between 100 mv to 600 mv. The redox potential values for the 3-cm and 6-cm depths fluctuated between 0 and 700 mv. The fluctuations in redox potential values during the length of overland flow experiment were highest for the untreated soil system followed by prereduced and limed treatments. The soil-plant system in the limed soil was the least reduced, apparently due to more vigorous plant and root growth resulting in more oxygen diffusion into the soil system. It is apparent from Figure 27 that soil systems in various treatments were more oxidized at the end of two-day break when no simulated wastewater was applied. This was mainly due to moisture loss by evapotranspiration. The soil system started getting more reduced with the influent application and reached maximum reduction on the fourth or fifth day of each five-day water application cycle.

It may be pointed out that the redox potential values are only an approximation of the oxidation-reduction conditions. The data presented in Table D-1 are averaged values of two electrodes installed at each soil depth while individual electrodes had a greater spread of values. Few individual redox potential values recorded were as low as -70 mv. A more intense reduction of the soil system results in the reduction of ferric hydroxide to ferrous hydroxide affecting phosphorus sorption, the implications of which will be discussed later in the section.

Efficiency of Phosphorus-32 Removal by Soil-Plant System in Overland Flow Model

The phosphorus-32 recovery in the combined runoff and subflow samples collected at the end of every influent application is plotted in Figure 28. The proportion of applied phosphorus-32 recovered in the effluent samples was lowest in the limed treatment followed by prereduced and untreated soils. The phosphorus-32 recovered in the effluents ranged between 0.4 to 6.5%, 4.8 to 35.3% and 16.0 to 60.8% of added phosphorus-32 in the limed, prereduced and untreated soils, respectively (Figure 28; Table D-2). An examination of the data plotted in

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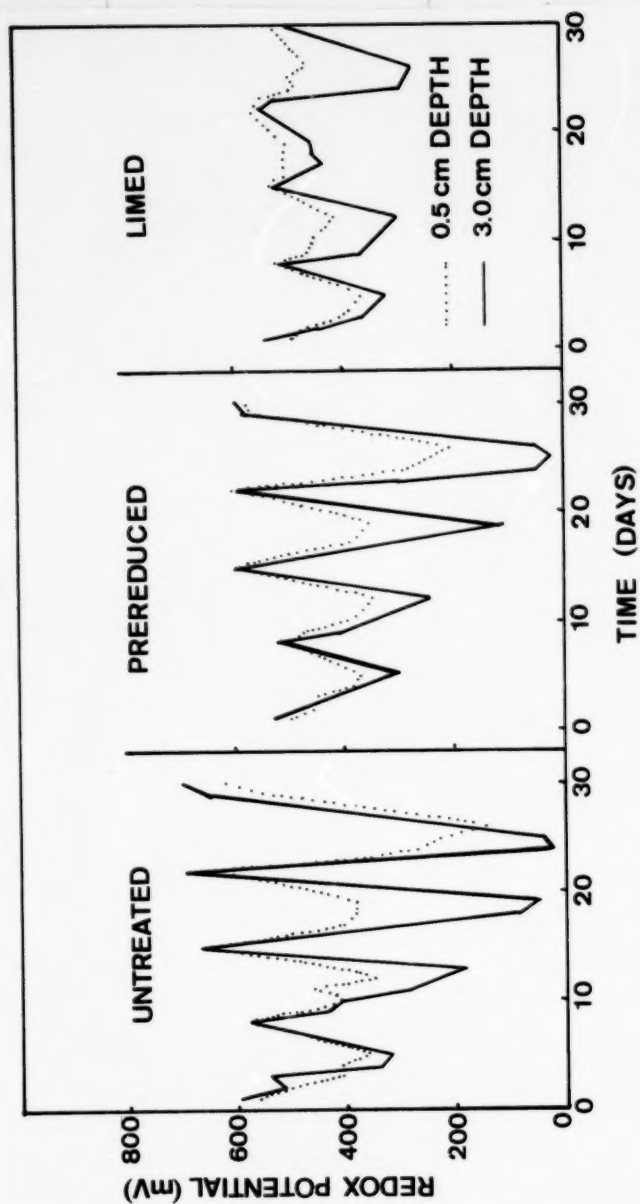


Figure 27. Redox potential measurements at two soil depths during overland flow treatment of simulated wastewater containing phosphorus-32 in Crowley soil-rye grass system.

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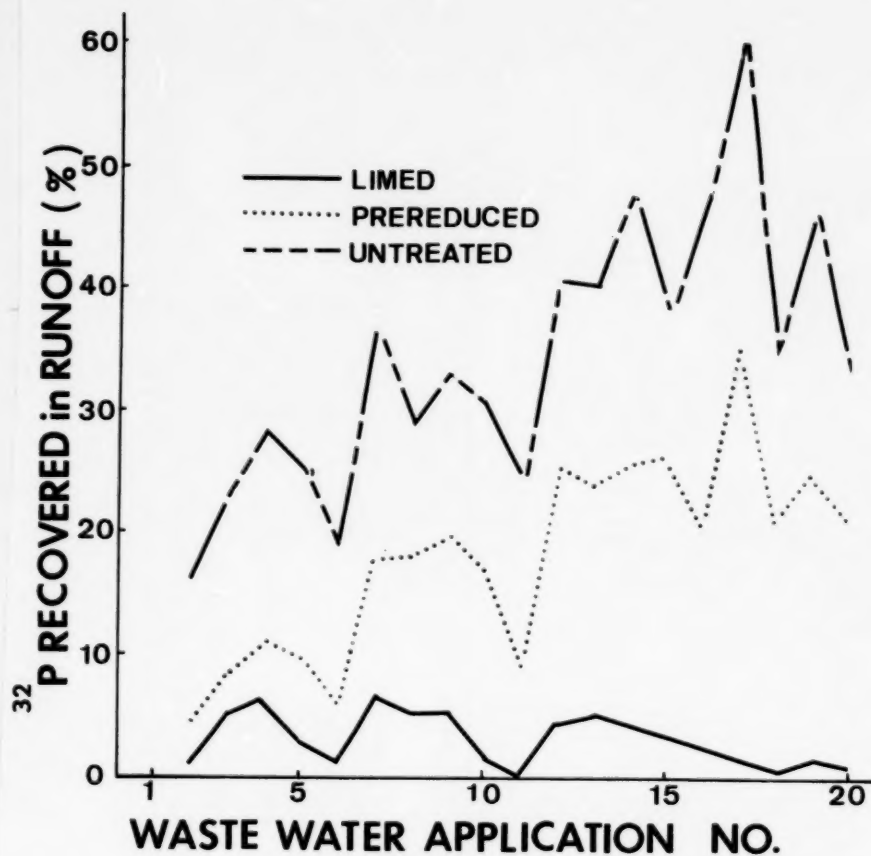
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Figure 28. Effect of soil pretreatments on the efficiency of phosphorus-32 removal from simulated wastewater in Crowley soil-rye grass system in an overland treatment model.

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Figure 28 show that the proportion of added phosphorus-32 recovered on the 6th, 11th, and 16th influent application decreased considerably. These applications were made after a two-day break which resulted in more water retained by the soil-plant system and hence less phosphorus-32 recovery in the runoff plus subflow fraction. The volumes of water collected in the runoff plus subflow effluent during the length of experiment are presented in Table D-3.

The overall recovery of added phosphorus-32 in the runoff plus subflow water was 3.2, 18.2, and 34.6% in the limed, pre-reduced and untreated soils, respectively. This means that 96.8% of added phosphorus-32 was retained by the soil-plant system in the limed soil followed by 81.8% in the prereduced and 65.4% in the untreated soil.

The applied phosphorus-32 not recovered in the runoff plus subflow effluents may be sorbed by the soil complex or taken up by the growing plants. The data summarized in Table 29 indicate that uptake of applied phosphorus-32 by the rye grass plants accounted for 14.4, 11.3, and 18.5% in the untreated, prereduced, and limed soils, respectively.

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TABLE 29. EFFECT OF SOIL PRETREATMENTS ON PHOSPHORUS-32 UPTAKE BY RYE GRASS IN AN OVERLAND FLOW TREATMENT OF WASTEWATER*

Distance downslope, cm	Treatments		
	untreated	prereduced	limed
	³² P uptake, % of added ³² P		
0-25	6.51	6.05	6.80
25-50	3.38	2.26	5.26
50-75	2.02	1.39	3.91
75-100	2.46	1.62	2.48
Total Uptake	14.37	11.32	18.45

* Data reported are average of 2 replications.

The balance sheet calculated for the applied phosphorus at the end of the experiment given in Table 30 indicates that added phosphorus-32 sorbed by the soil complex was in the order of:

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TABLE 30. MASS BALANCE OF APPLIED PHOSPHORUS-32 RECOVERED AT THE END OF OVERLAND FLOW EXPERIMENT IN CROWLEY SOIL-RYE GRASS SYSTEM

System component	Treatments		
	untreated	prerduced	limed
	³² P recovered, %		
³² P added	100	100	100
Runoff plus subflow	34.65	18.25	3.21
Plant uptake	14.37	11.32	18.45
Remaining in soil	50.98	70.43	78.34

Distribution of Sorbed Phosphorus-32 Fraction as a Function of Soil Depth and Downslope Distance

Three soil phosphorus fractions were determined in the soil samples collected at the end of overland flow treatments:

Soluble Phosphorus-32 Fraction--

Soil was extracted with 0.01 M calcium chloride solution and the activity of phosphorus-32 was counted in the filtrates. This fraction represents phosphorus that can easily desorb and leach out of the soil system.

Plant Available Phosphorus-32 Fraction--

The residual soil from the calcium chloride extraction was extracted with 0.5 M sodium bicarbonate solution and the activity of phosphorus-32 in the filtrates was determined. Fractions one and two were combined together and are referred to as sodium bicarbonate fraction. This extraction has been shown to be significantly correlated to the uptake of phosphorus by growing plants and reflects the plant-available fraction (Olsen and Watanabe, 1954; Colwell, 1963; Bar-Yosef and Akiri, 1978).

Total Soil Phosphorus-32 Fraction--

An estimate of phosphorus-32 sorbed by the soil complex was determined by analyzing the soil samples collected from various depths and distances downslope for total phosphorus.

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The data on various soil fractions is summarized in Table 31. The total soil phosphorus-32 is expressed as counts/minute/g of soil while fractions one and two are expressed as percent of total phosphorus-32 recovered in the respective soil samples.

The distribution of total phosphorus-32 sorbed by the soil complex was influenced by soil pretreatments. For example, in the limed treatment the highest phosphorus-32 activity was observed in the 0- to 2-cm soil depth which decreased with distance downslope. The phosphorus-32 activity decreased in the 2- to 4-cm depths and again increased in the 4- to 8-cm soil depth. This trend was observed in all four sections downslope. In the prereduced and untreated soil systems the total phosphorus-32 activity increased with depth and this pattern was observed in all soil sections downslope.

Soluble phosphorus-32 desorbed with calcium chloride from the soil complex ranged from 0 to 0.3% of total sorbed phosphorus-32 in the untreated and prereduced soil treatments and from 0.1 to 1.2% in the limed treatment. These values indicate that very little of the sorbed phosphorus was present in the soluble fraction which was subject to leaching losses.

Plant available fractions ranged from 21.1 to 53.7% in the limed soil, 11 to 38.0% in the prereduced treatment and 7.2 to 25.4% in the untreated soil system. The fraction of sorbed phosphorus present in the plant available form generally decreased with downslope distance in the 0- to 2-cm soil layer only. No consistent trends with depth or downslope distance were observed otherwise.

Soil pH

The pH data for soil samples collected at the end of the overland flow treatments are prescribed in Table D-4. The pH values ranged from 6.0 to 6.3 in the untreated soil, from 6.5 to 6.9 in the prereduced soil, and from 7.2 to 7.7 in the limed soil. The pH values of prereduced soil samples were closer to neutrality than the untreated soil due to longer equilibration time under flooded soil conditions prior to application of overland flow treatments. Higher pH values in the limed soil was because of calcium carbonate application at the start of the experiment. In the limed treatment, pH values of soil samples increased slightly with distance downslope. No consistent trend in pH values with depth was observed in any treatment.

Effect of Soil Pretreatments on Sorption-Desorption Behavior of Phosphorus Under Laboratory Conditions

Phosphorus sorption isotherms were determined in Crowley soil which was incubated for 13 weeks under various soil pretreatments identical to the overland flow experiments described earlier.

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TABLE 31. DISTRIBUTION OF SORBED PHOSPHORUS-32 IN VARIOUS SOIL FRACTIONS AS A FUNCTION OF DISTANCE DOWNSLOPE AND SOIL DEPTH DETERMINED AT THE END OF OVERLAND FLOW TREATMENTS IN CROWLEY SOIL-RYE GRASS SYSTEMS*

Distance downslope, cm	Soil depth, cm	Treatments											
		untreated						prereduced					
		total 32P cpm/g	CaCl ₂ - 32P %	NaHCO ₃ - 32P %	total 32P cpm/g	CaCl ₂ - 32P %	NaHCO ₃ - 32P %	total 32P cpm/g	CaCl ₂ - 32P %	NaHCO ₃ - 32P %	total 32P cpm/g	CaCl ₂ - 32P %	NaHCO ₃ - 32P %
0-25	0-2	4866	0.1	16.1	4672	0.3	31.2	12607	1.0	53.7			
	2-4	5269	0.1	14.5	9065	0.1	11.1	3838	0.2	27.9			
	4-8	9833	0.2	23.4	10279	0.1	19.4	4932	0.1	21.1			
25-50	0-2	1548	0.1	13.2	524	0.3	25.3	8920	0.4	44.4			
	2-4	1683	0.2	25.4	3382	0.2	38.0	3022	0.3	27.6			
	4-8	1618	0.0	15.5	6906	0.0	14.2	5180	0.3	36.7			
50-75	0-2	564	0.2	17.2	244	0.0	22.1	7857	0.3	21.2			
	2-4	1735	0.1	25.1	1149	0.1	14.8	1708	0.2	32.2			
	4-8	2780	0.1	15.6	5907	0.0	17.7	4083	0.2	24.4			
75-100	0-2	1443	0.1	7.2	288	0.4	13.9	7725	1.2	22.5			
	2-4	3711	0.1	17.3	2175	0.0	23.4	452	0.4	25.2			
	4-8	5606	0.1	14.9	10555	0.1	15.6	892	0.1	28.3			

* Data presented are average of 2 replications.

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The experimental data for phosphorus added and that received in the equilibrium solution after 24 hours of shaking are presented in Table D-5. The plot of phosphorus sorbed against the concentration of phosphorus remaining in solution indicates that in the low phosphorus sorption range ($< 100 \mu\text{g}$ phosphorus/g), the difference between the three soil pretreatments was negligible (Figure 29). At higher sorbed phosphorus levels the magnitude of phosphorus retained by the soil complex was in the order of:

Prerduced $<$ Limed $<$ Untreated

However, a relatively steeper slope of limed soil compared to prerduced and untreated soils at the higher levels of solution phosphorus indicates that the phosphorus sorption capacity of limed treatments in this range may be greater than the unlimed soil treatments.

The fraction of phosphorus retained by the soil complex was desorbed by two subsequent extractions with calcium chloride and the percentage of sorbed phosphorus desorbed was calculated. The data plotted in Figure 30 indicate that the fraction of sorbed phosphorus desorbed with calcium chloride was lowest in the prerduced soil treatment. This indicated that phosphorus retained by the soil complex in the prerduced treatments was more tightly held or the compounds formed had lower solubilities and thus would be less subject to leaching losses. The percent recovery of sorbed phosphorus in the limed treatment was higher than that in the untreated soil up to sorbed phosphorus level of $300 \mu\text{g}$ phosphorus/g. At higher levels of sorbed phosphorus, the two curves crossed over with the highest concentration of desorbed phosphorus present in the untreated soil. The cumulative desorption values for both the extractions are plotted in Figure 31, which indicates similar desorption behavior as presented in Figure 30.

Phosphorus Sorption Parameter Calculated From Langmuir Two-Surface Equation

Labile phosphorus values were added to the experimentally determined phosphorus sorbed fraction for computing various parameters using the Langmuir Two-Surface equation. The calculated values summarized in Table 32 indicate that phosphorus sorption energy was highest for the prerduced soil followed by untreated and limed soils. Much larger k' values compared to insignificantly small k'' suggest that most of the phosphorus sorbed in the low concentration range was associated with high energy sorption sites. Very low $k' + k''$ values in the limed soil treatment indicate the sorbed phosphorus may not be held

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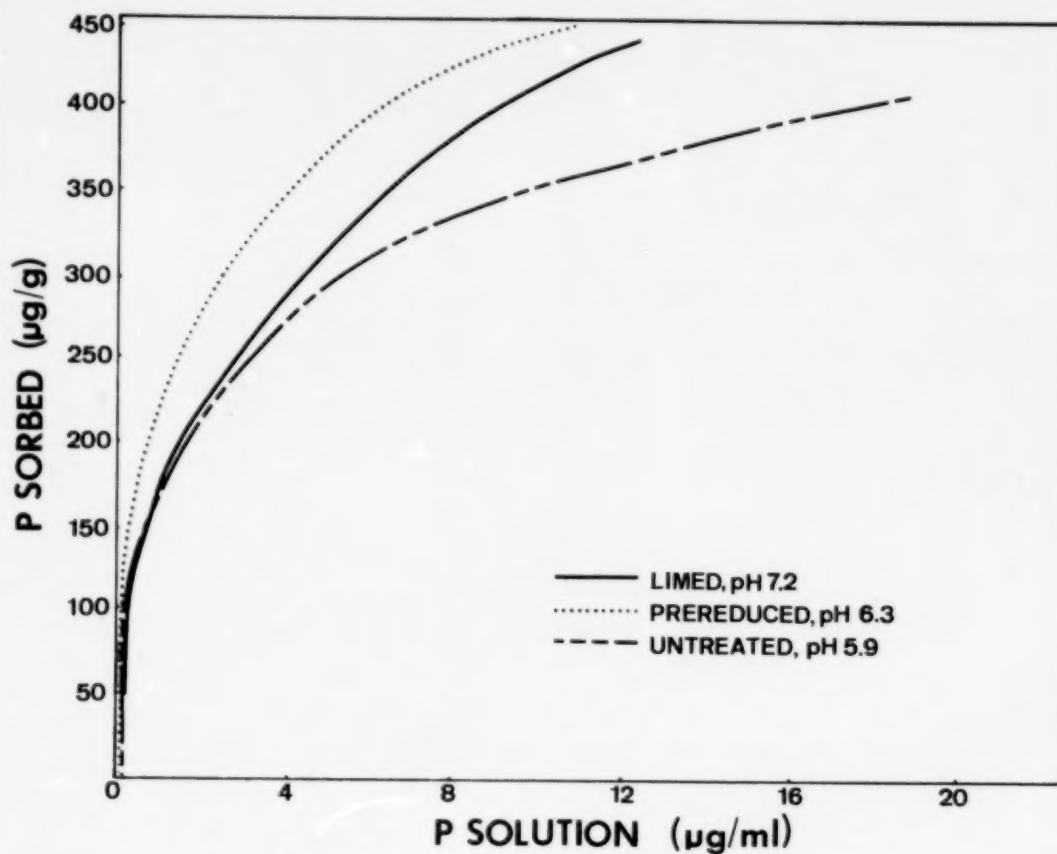


Figure 29. Effect of soil pretreatments on phosphorus sorption in Crowley soil determined in 1:5 soil - 0.01 M calcium chloride suspensions.

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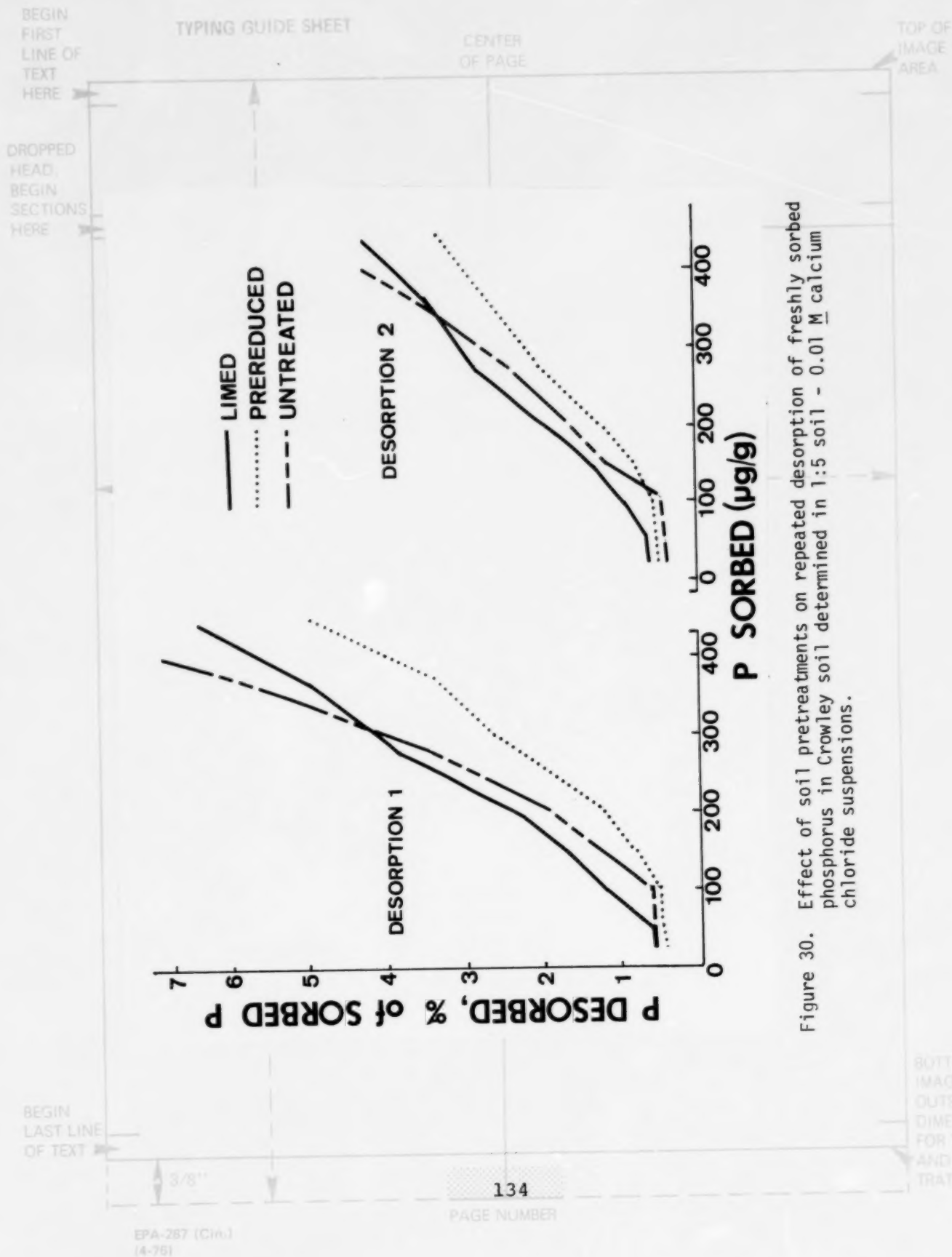


Figure 30. Effect of soil pretreatments on repeated desorption of freshly sorbed phosphorus in Crowley soil determined in 1:5 soil - 0.01 M calcium chloride suspensions.

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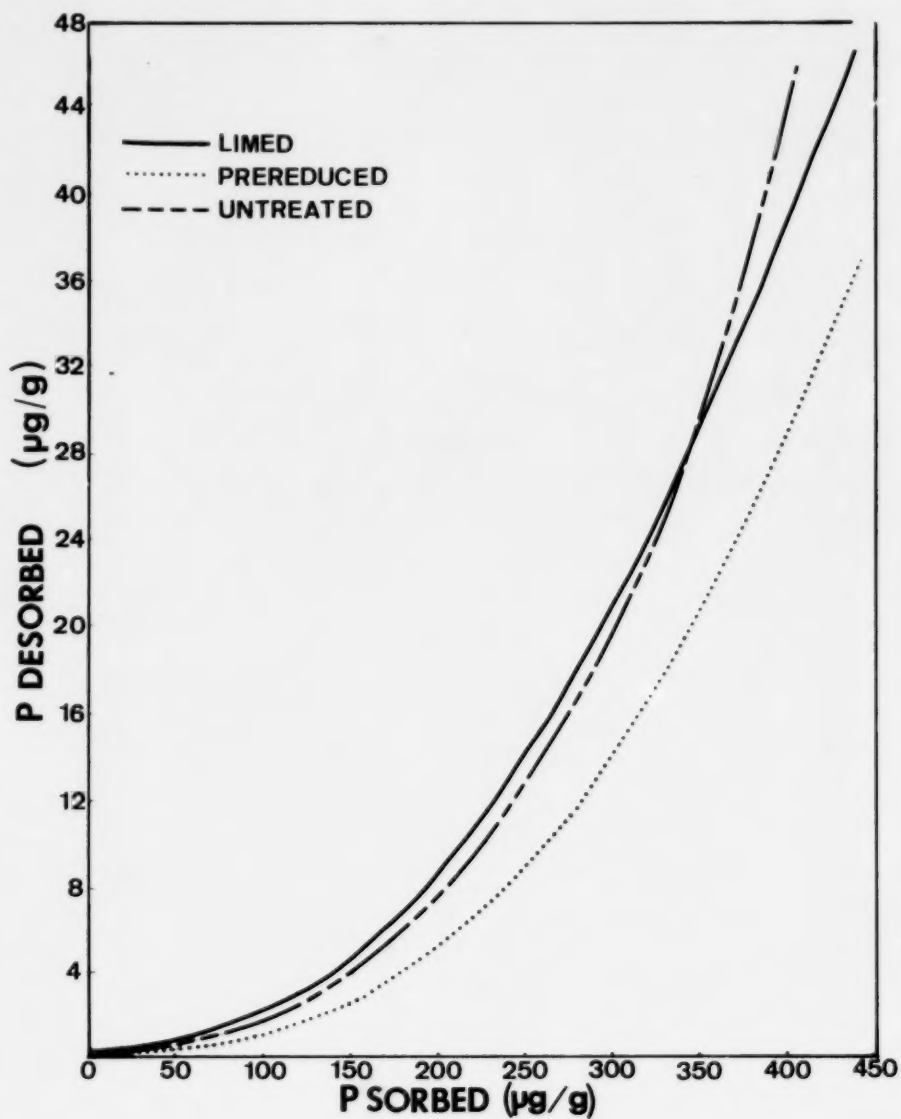
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Figure 31. Effect of soil pretreatment on cumulative phosphorus desorption (Des 1 and Des 2) in Crowley soil determined in 1:5 soil - 0.01 M calcium chloride suspensions.

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TABLE 32. EFFECT OF SOIL PRETREATMENTS ON LABILE PHOSPHORUS, AND VARIOUS PHOSPHORUS SORPTION PARAMETERS CALCULATED FROM LANGMUIR TWO-SURFACE EQUATION

Variable		Treatments		
		untreated soil	prerduced soil	limed soil
P conc. at zero P added (µg/ml)		0.012	0.012	0.035
Labile P (µg/g)		18.070	39.900	17.090
P sorption energy (ml/µg P) *		18.730	32.090	4.850
P sorption capacity (µg/g) **		504	548	703
P buffer capacity (ml/g)		2693	5314	852
	k'	18.570	31.790	4.760
	k"	0.160	0.300	0.090
Sorption parameters	X' _m	141.800	163.320	168.790
	X" _m	379.360	421.790	551.530

* values for $k' + k''$

** values for $(X'_m + X''_m)$ -labile P

very tightly and that the mechanism of sorption may be different from that of untreated and prerduced soil where no lime was added.

Phosphorus sorption capacity (X_m) of limed soil calculated from the Langmuir equation was highest followed by prerduced and untreated soils (Table 32). This difference in phosphorus sorption capacity was mainly due to the low-energy sorption surfaces (X''_m). This may indicate that liming Crowley soil would tremendously increase the phosphorus sorption capacity but a larger fraction of this sorbed phosphorus would be loosely bound.

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The results of the overland flow experiment and phosphorus sorption parameters derived from the laboratory sorption data using the Langmuir equation indicated that liming Crowley soil with calcium carbonate to raise the soil pH above 7.0 resulted in maximum retention of added soluble phosphorus followed by prereduced and untreated soil samples. The presence of excess calcium carbonate (60 milliequivalents/100 g soil) in the soil apparently resulted in the precipitation of added phosphorus as calcium phosphate thus removing phosphorus from solution. Several calcium compounds with varying solubilities have been reported to be formed with phosphate under alkaline soil conditions. Some of the important calcium phosphate compounds formed after reaction with calcium carbonate that limit orthophosphate solubility in soils are calcium phosphate $[\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}]$, tricalcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$, octacalcium phosphate $[\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}]$, and hydroxyapatite $[\text{Ca}_5\text{OH}(\text{PO}_4)_3]$. The negatively increasing solubility product constants (-pk sp of 6.56, 26.0, 46.91, and 55.60, respectively) for the compounds listed above suggest decreasing solubility with increased calcium reaction and hence more retention of added phosphate (Moreno et al., 1960; Stumm and Morgan, 1970; Enfield and Bledsoe, 1975; Subbarao and Ellis, 1977).

Holford and Mattingly (1975a) proposed that sorption of potassium phosphate (KH_2PO_4) on limestone was due to initial chemisorption reaction at low solution phosphate concentrations followed by physical adsorption of low bonding energy and finally precipitation probably as octacalcium phosphate in solution and its deposition on the adsorbed layer. The reactions between calcium carbonate and phosphate ions are kinetic and much phosphate is adsorbed rapidly on the surface as a monolayer, though the amounts adsorbed and the equilibrium concentration of phosphate vary with the surface area of calcium carbonate used (Mattingly, 1975). Kuo and Lotse (1972) described the adsorption process as competition between phosphate and adsorbed water molecules, bicarbonate ions or hydroxyl ions, the relative adsorption of which depend on the solubility product of the compound formed on the surface. The negative logarithm of the solubility product (-pk sp) of calcium phosphate $[\text{CaHPO}_4]$, the most soluble of the calcium phosphate compounds formed is 6.56 compared to 5.43 and 1.2 for calcium hydroxide $[\text{Ca}(\text{OH})_2]$ and calcium bicarbonate $[\text{CaHCO}_3]$, respectively, indicating that phosphate ions will be more strongly adsorbed than hydroxyl or bicarbonate ions. The 96.8% sorption of added phosphorus in the limed treatments during four weeks of overland flow treatment may be a combined effect of monolayer adsorption as well as calcium phosphate precipitation during experimental period. Adsorption by hydrous oxides in the limed treatments may not

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play a significant role due to insignificant dissolution of iron compounds in the pH range of 7.1 to 7.7 as discussed earlier in Section 5.

The phosphorus removal efficiency of prereduced and untreated soil models in the overland flow treatment was 81.8 and 65.3%, respectively. Since no calcium carbonate was added to Crowley soil in these two treatments the adsorption of added phosphorus may involve ferric phosphate $[\text{FePO}_4]$ as well as ferrous phosphate $[\text{Fe}_3(\text{PO}_4)_2]$ precipitation, adsorption by reprecipitated ferrous hydroxide $[\text{Fe}(\text{OH})_2]$ and sorption on soil exchange sites. The redox potential measurements in these two unlimed treatments fluctuated between -70 mv to over +600 mv suggesting conversion of ferric ions. In the prereduced treatment the soil was allowed to equilibrate under waterlogged conditions for 13 weeks prior to the addition of soluble phosphate during overland flow treatment which may have resulted in more iron converted from ferric oxides to ferric hydrous oxides than in the untreated soil thus increasing phosphorus sorption (Khalid et al., 1977). The laboratory data indicate that phosphorus sorption capacity ($X' + X''$) of prereduced soil was greater than that of untreated soil (548 vs 504 μg phosphorus/g; Table 32). The laboratory study, therefore confirms the overland flow data such that a longer period of anaerobiosis resulted in a greater efficiency of phosphorus removal.

The phosphorus sorption energy ($k' + k''$) calculated from the Langmuir isotherm was highest in the prereduced treatment followed by untreated and limed soils (Table 32). Essentially all of the sorption energy was contributed by the high energy sorption sites (k') and the contribution of low energy sorption sites (k'') was negligible. The very low sorption energy of limed soil compared to untreated and prereduced soils (4.85 vs 18.73 and 32.09 ml/ μg phosphorus) suggests that sorbed phosphorus in limed treatments would be easily desorbed. The desorption of freshly sorbed phosphorus with calcium chloride solution in the laboratory also demonstrates a greater desorption of sorbed phosphates in the limed treatments up to 325 μg phosphorus/g sorbed phosphorus but the magnitude of difference was not great (Figures 30, 31). This trend of greater phosphorus desorption in the limed treatments than the other two treatments was further evident in the overland flow experiment where comparatively more sorbed phosphorus was desorbed with calcium chloride as well as sodium bicarbonate extractions in the limed soil samples extracted at the end of experiment. Plant uptake of added phosphorus was also higher in the limed treatments compared to the untreated and prereduced soil treatments where no lime was added.

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The results of the overland flow experiment conducted on Crowley silt loam-rye grass system established at 1.2% slope demonstrate that the efficiency of phosphorus removal from municipal wastewater would be greatly enhanced by addition of lime (calcium carbonate) to the soil. The prereduction of soil-plant system for extended period of time may also result in more phosphorus removal than less-reduced non-limed soil. The phosphorus sorption isotherms conducted in the laboratory on the pretreated soils and the sorption parameters computation by the Langmuir two-surface equation demonstrated that the efficiency of phosphorus removal in the overland flow experiment was related to the phosphorus sorption capacity of various treatments. A slightly higher desorption of phosphorus sorbed in the overland flow as well as laboratory studies in the limed treatments was due to the lower phosphorus bonding energy in this treatment. Phosphorus sorbed under alkaline conditions was more available to growing plants than the unamended treatments. The results of this study also suggest that phosphorus sorption is a kinetic process and that the leaching losses of phosphorus retained by the soil mass during overland flow application would be smaller due to the longer reaction time as compared to the desorption potential determined in the laboratory.

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TABLE A-1. RATE OF WATER RUNOFF AND SUBFLOW (ML/MINUTE) THROUGH A MOON SOIL-RYE GRASS SYSTEM IN AN OVERLAND FLOW TEST MODEL ADJUSTED TO 2.2% SLOPE. TOTAL VOLUME OF WATER APPLIED = 9.3 L/DAY (EQUIVALENT TO 2-CM DEPTH)

Days water applied*				APPENDIX A			
1		2		3			
time, minutes	runoff	subflow	time, minutes	runoff	subflow	time, minutes	runoff
20	0.00	0.00	21	0.00	0.00	30	0.00
30	3.20	0.00	31	3.75	0.00	40	0.00
40	7.70	4.00	41	5.90	1.10	50	2.30
50	9.00	5.10	51	7.70	4.70	60	7.10
60	10.50	3.50	61	7.00	4.70	100	3.15
90	16.07	4.83	91	10.83	6.50	130	2.77
120	17.00	5.50	121	14.00	7.60	160	2.77
150	17.83	6.67	151	15.17	8.00	190	2.67
180	18.00	6.33	181	16.00	5.67	220	2.78
210	17.67	6.67	211	16.83	6.83	240	3.07
240	19.83	7.00	247	17.36	6.19	280	3.90
270	17.67	6.83	271	17.29	6.33	310	3.33
300	17.83	7.00	301	17.67	5.00	340	2.93
323 [†]	17.83	7.83	339 [†]	17.89	6.05	390	3.40
333	10.20	5.10	349	10.50	5.10	425 [†]	3.00
343	1.00	6.30	359	1.10	5.40	435	4.50
353	0.00	3.00	369	0.00	2.36	449	2.07
363	0.00	3.20	379	0.00	2.55	463	0.25
463	0.00	1.12	479	0.00	0.70	553	0.44

(Continued)

*Average water input rate = 29.8 ml/minute. [†]Time total water input pumped in.

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TABLE A-1 (Continued)

5 ^f			Days water applied* 6			7		
time, minutes	runoff	subflow	time, minutes	runoff	subflow	time, minutes	runoff	subflow
20	0.00	0.00	15	0.00	0.00	13	0.00	0.00
30	4.10	0.00	25	11.50	0.00	25	8.33	0.00
40	8.50	0.00	35	11.50	0.00	35	14.00	0.00
50	11.50	0.00	48	19.61	0.00	45	16.00	0.00
60	15.00	0.00	67	20.00	1.09	55	17.50	1.83
90	12.50	3.30	97	20.00	1.77	85	18.71	2.61
120	16.00	4.17	127	22.50	3.67	115	20.33	3.83
150	17.67	4.17	157	23.33	3.77	145	24.00	3.33
180	19.67	4.67	192	22.57	3.43	175	23.33	3.33
230	19.10	4.40	222	24.33	3.50	226	23.72	3.43
260	22.33	3.50	278 [†]	24.28	3.66	256	23.00	4.67
285 [†]	20.80	3.72	291 [†]	23.46	3.23	290	26.47	6.47
295	14.50	3.40	302	12.73	3.36	305	11.54	3.33
305	0.65	2.00	312	0.90	1.45	315	1.00	1.60
310	0.40	1.25	322	0.25	1.00	325	0.50	2.30
430	0.00	0.17	432	0.00	0.29	445	0.00	0.48

*Average water input rate = 29.8 ml/minute. †No water applied on fourth day. ‡Time total water input pumped in.

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TABLE A-2. THE EFFECT OF SLOPE ON THE RATE OF WATER RUNOFF AND SUBFLOW (ML/MINUTE) THROUGH A MOON SOIL-EYE GRASS SYSTEM IN AN OVERLAND FLOW TEST MODEL (TOTAL VOLUME APPLIED, 9.3 L; EQUIV. 2 CM DEPTH)*

Slope											
1.1%			2.2%			3.3%			4.4%		
time, minutes	runoff	subflow	time, minutes	runoff	subflow	time, minutes	runoff	subflow	time, minutes	runoff	subflow
23	0.00	0.00	17	0.00	0.00	13	0.00	0.00	14	0.00	0.00
35	12.67	0.00	28	8.36	5.27	23	14.00	0.00	24	19.00	0.00
45	17.00	0.00	38	14.50	6.90	33	20.00	1.00	37	13.85	8.77
57	15.00	0.00	48	17.00	6.00	43	21.00	0.90	54	12.35	11.18
85	10.18	1.14	58	19.50	2.10	55	18.33	1.54	74	15.00	6.50
127	15.24	8.57	105	18.51	4.57	117	20.89	2.58	96	18.64	4.09
137	19.00	5.72	133	18.39	5.18	150	21.51	2.48	144	18.54	4.27
190	19.49	5.94	164	18.55	6.45	190	23.00	2.07	190	21.29	3.55
217	20.37	5.74	194	18.17	5.00	240	22.90	1.80	222	22.50	1.97
257	20.00	6.00	203	19.31	5.52	275	24.57	1.91	271	23.51	1.06
306 [†]	19.49	6.12	274	21.08	5.20	315 [†]	23.00	1.52	314	23.25	0.46
316	13.00	4.80	312 [†]	20.26	4.34	325	12.50	1.50	329	25.12	0.40
328	3.17	1.08	322	11.50	3.30	335	1.10	0.90	340	11.50	0.35
338	1.50	0.40	332	1.70	0.60	345	0.80	0.30	350	0.80	0.00
448	0.19	0.09	448	0.03	0.07	448	0.00	0.00	448	0.00	0.00

*Average water input rate = 29.47 ml/minute. [†]Time total water input pumped in.

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APPENDIX B

TABLE B-1. EFFECT OF SOIL DEPTH AND MODEL DISTANCE ON REDOX POTENTIAL (MV) LEVELS WITH TIME (MOON SOIL,
EXPERIMENT 1)

Application No.	Date	Distance downslope, cm											
		19				57				95			
		0.5	3.0	6.0	0.5	3.0	6.0	0.5	3.0	6.0	0.5	3.0	6.0
1	3/26	542.0	187.0	234.5	609.5	202.0	337.0	567.0	162.0	209.5	504.5	617.0	479.5
2	3/27	599.5	204.5	207.0	382.5	212.0	274.5	562.0	72.0	179.5	537.0	687.0	472.0
3	3/29 †	592.0	174.5	149.5	592.0	149.5	109.5	497.0	-85.5	82.0	549.5	597.0	232.0
4	3/30	594.5	267.0	147.0	607.0	174.5	192.0	539.5	-33.0	74.5	554.5	662.0	232.0
5	3/31	579.5	189.5	114.5	602.0	139.5	207.0	562.0	-108.0	89.5	474.5	604.5	164.5
6	4/1	577.0	204.5	92.0	652.0	332.0	139.5	539.5	-125.5	34.5	542.5	659.5	199.5
7	4/2	562.0	199.5	67.0	657.0	234.5	69.5	534.5	-160.5	-15.5	527.0	622.0	522.0
8	4/3	567.0	209.5	47.0	677.0	284.5	114.5	557.0	-138.0	23.0	562.5	639.5	217.0
9	4/4	562.0	262.0	27.0	687.0	374.5	154.5	599.5	170.5	-30.5	579.5	644.5	227.0
10	4/5	597.0	487.0	49.5	687.0	529.5	309.5	604.2	-165.5	-38.0	602.0	687.0	347.0
11	4/6	614.5	484.5	77.0	689.5	522.0	339.5	627.5	95.5	55.5	547.0	634.5	269.5
12	4/7	607.0	512.0	134.5	697.0	539.5	339.5	642.0	-130.5	-10.5	602.0	562.0	259.5
13	4/8	599.5	512.0	152.0	684.5	552.0	342.0	654.5	22.0	-73.0	617.0	509.5	247.0
14	4/9	624.5	694.5	192.0	697.0	674.5	334.5	669.5	122.0	-78.0	564.5	692.0	482.0
15	4/10	562.0	687.0	252.0	689.5	664.5	327.0	662.0	132.0	-93.0	637.0	569.5	477.0
16	4/11	587.0	692.0	262.0	682.0	669.5	332.0	647.0	162.0	-98.0	654.5	539.5	264.5
17	4/12	577.0	694.5	272.0	692.0	682.0	367.0	641.0	230.0	-70.0	607.5	585.0	305.0
18	4/13	552.0	707.0	284.5	694.5	697.0	412.0	647.0	357.0	-33.0	582.0	674.5	409.5
19	4/14	572.0	702.0	633.0	689.5	674.5	424.5	667.0	307.0	-20.5	629.5	637.0	374.5
20	4/15	559.5	697.0	312.0	677.0	677.0	429.5	684.5	304.5	-43.0	617.0	507.0	299.5
21	4/16	619.5	704.5	329.5	692.0	697.0	454.5	694.5	529.5	37.0	667.0	649.5	382.0
22	4/17	597.0	712.0	359.5	699.5	697.0	487.0	694.5	612.0	224.5	647.0	684.5	487.0
23	4/18	599.5	704.5	369.5	697.0	682.0	484.5	689.5	597.0	204.5	689.5	642.0	384.5
24	4/19	617.0	709.5	387.0	689.5	692.0	487.0	647.0	607.0	204.5	682.0	634.5	367.0
25	4/20	617.0	704.5	382.0	697.0	674.5	477.0	684.5	532.0	137.0	679.5	592.0	362.0
26	4/21	549.5	714.5	394.5	679.5	702.0	512.0	694.5	649.5	509.0	647.0	722.0	554.5

† Started applying nitrogen-15 in influent.

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TABLE B-2. EFFECT OF SOIL DEPTH AND MODEL DISTANCE ON SOIL NITROGEN DETERMINED AFTER RYE GRASS HARVEST (MOON SOIL, EXPERIMENT 1)

Distance downslope cm	Ammonium-nitrogen			Nitrate-nitrogen soil depth, cm			Organic-nitrogen		
	µg N/g			µg N/g			mg N/g		
	0 - 2.5	2.5 - 5.5	5.5 - 11	0 - 2.5	2.5 - 5.5	5.5 - 11	0 - 2.5	2.5 - 5.5	5.5 - 11
0-37	49.360	4.360	2.470	35.075	8.745	7.790	1.133	1.127	1.105
37-74	50.865	2.300	2.145	34.275	7.650	6.925	1.224	1.363	1.099
74-111	27.565	1.950	1.490	24.960	7.085	7.820	1.177	1.093	1.101
111-148	41.820	2.095	2.655	34.580	10.350	7.750	1.221	1.118	1.085
Pretreatment	6.780			6.540			1.156		
Soil	6.600			6.642			1.142		

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TABLE B-3. RECOVERY OF NITROGEN GAS (N_2) AS DETERMINED BY MASS SPECTROMETRIC ANALYSIS OF GASEOUS ATMOSPHERE IN MHOON SOIL AND GRENADA SOIL-PLANT SYSTEM IN A SEALED GROWTH CHAMBER

Time, days	Mhoon soil			Grenada soil
	100 mg N/g	150 mg N/g	NH ₄ ⁺ - ¹⁵ N added	150 mg N/g
			200 mg N/g	
¹⁵ N recovered, mg				
First cycle *				
0.3	2.38	0.00	1.80	0.30
3	21.27	21.43	33.06	0.34
5	32.31	18.05	25.64	0.50
8	39.47	33.74	15.67	0.69
11	28.95	38.78	12.15	1.46
Second cycle *				
0.3	0.00	0.00	0.00	0.00
3	1.28	1.76	8.41	1.66
6	4.61	3.53	5.48	2.99
8	4.31	5.27	6.15	4.50

* Soil-plant system was maintained at 25% moisture (30% for Grenada Soil) for 8 days prior to increasing the moisture level to 50% for denitrification to occur. No nitrogen-15 gas was detected in the 25% moisture level incubation. First and second cycles refer to incubation at 50% moisture.

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TABLE B-4. RECOVERY OF NITROGEN GAS AS DETERMINED BY MASS SPECTROMETRIC ANALYSIS OF GASEOUS ATMOSPHERE IN GRENADA SOIL - RYE GRASS SYSTEM IN A SEALED GROWTH CHAMBER

Time, days	N treatment*	
	$\text{NO}_3^- \text{-N}$	$\text{NH}_4^+ \text{-N}$
¹⁵ N recovered, mg N		
Reduction cycle 1**		
0	0.00	0.00
2	2.68	2.55
4	24.36	22.58
6	16.93	14.96
8	17.10	15.83
10	17.70	19.35
13	17.98	17.22
Reduction cycle 2**		
0	0.00	0.00
3	17.22	10.21
5	17.15	8.83
7	36.20	20.51
8	26.90	15.59
10	24.59	15.91
12	28.70	15.48

* 600 mg ¹⁵N was applied at the start of the experiment.

** Each reduction cycle was preceded by an oxidation cycle. See Table 15 for experimental details.

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TABLE B-5. EFFECT OF NITROGEN FORMS AND PLANT GROWTH ON THE RECOVERY OF APPLIED LABELLED NITROGEN IN COMBINED RUNOFF AND SUBFLOW IN MHON SOIL OVERLAND FLOW MODEL

Influent #	Treatments									
	NH_4^+-N					NO_3^--N				
	without plants		with plants			without plants		with plants		
	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N	^{15}N recovered, $\mu\text{g N as NH}_4^+-\text{N}$	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N
1	12.5	1.0	11.5	0.0	39.7	78.0	40.3	0.0		
2	274.1	10.2	191.6	0.0	518.8	969.8	15.2	1862.9		
3	159.7	7.5	388.3	21.8	714.6	1978.3	334.0	265.0		
4	1070.1	27.9	304.3	0.0	0.0	2578.8	19.2	543.6		
5	4.9	1.3	2.1	0.0	21.6	58.6	0.0	6.7		
6	387.5	0.0	2399.5	78.8	1.7	0.0	8.7	292.5		
7	304.7	0.0	680.4	4.0	58.6	846.5	17.7	0.0		
8	0.0	0.0	0.0	0.0	0.0	0.0	8.3	793.6		
9	2.6	0.0	12.2	3.6	5.5	0.0	5.6	129.3		
10	666.3	5.2	20.9	0.0	45.1	61.0	8.3	0.0		
11	228.8	1.5	295.1	3.6	4.0	0.0	0.0	124.4		
12	0.0	0.0	733.2	28.4	14.2	21.2	0.8	332.5		
13	0.0	0.0	60.0	7.2	0.0	9.7	6.3	9.4		
14*	15.1	3.4	2.59	1.1	5.6	6.3	2.6	0.0		
15*	0.0	0.0	5.26	0.8	0.0	0.0	0.0	0.0		

*Distilled water was added only

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TABLE B-6. EFFECT OF PLANT GROWTH ON SOIL pH IN MHOON SOIL MEASURED AT THE END OF OVERLAND FLOW TREATMENTS

Depth cm	Distance downslope, cm							
	0 - 12.5	12.5 - 25	25 - 37.5	37.5 - 50	0 - 12.5	12.5 - 25	25 - 37.5	37.5 - 50
	$\text{NH}_4^+\text{-N}$, without plants				$\text{NH}_4^+\text{-N}$, with plants			
0-4	7.40	7.50	7.50	7.55	7.45	7.65	7.65	7.65
4-8	7.40	7.45	7.50	7.45	7.55	7.55	7.60	7.65
	$\text{NO}_3^-\text{-N}$, without plants				$\text{NO}_3^-\text{-N}$, with plants			
0-4	7.50	7.70	7.65	7.65	7.70	7.85	7.80	7.55
4-8	7.50	7.55	7.60	7.55	7.65	7.60	7.65	7.45

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TABLE C-1. EXPERIMENT 1. SUMMARY OF EXPERIMENTAL RESULTS FOR EFFECTS OF REDUCTION ON PHOSPHATE SORPTION ISOTHERMS

Redox potential (mv)	-150	+65	+500	untreated
Days of incubation	27	27	22	0
Final pH	6.6	5.9	5.2	5.6

Phosphate Sorption ($\mu\text{g P/g soil}$)

Initial P conc. * $\mu\text{g/ml}$	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x
0.03	0.017	255	0.004	18	0.003	16	0.007	34
3.88	0.019	280	0.014	41	0.018	40	0.011	57
7.75	0.021	302	0.075	64	0.106	63	0.042	80
15.50	0.024	349	0.481	108	0.596	106	0.333	124
23.25	0.070	394	1.440	148	1.770	145	0.985	168
31.00	0.133	438	3.090	183	3.630	179	2.240	207
46.50	0.327	527	7.980	245	9.400	237	6.730	273
62.00	0.673	613	15.400	293	17.600	279	13.500	325
77.50	1.340	699	24.100	329	26.900	315	22.700	363

Iron and Manganese Analyses ($\mu\text{g/ml}$)

	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
0.03	tr	>50	tr	10.5	0.3	0.7		
3.88	0.1	>40	0.2	8.4	0.1	0.2	0.1	3.8
7.75	0.2	>40	tr	9.6	0.1	0.2	0.2	3.5
15.50	0.1	>40	tr	12.3	0.1	0.2	0.1	3.7
23.25	0.1	>40	tr	13.9	0.1	0.3	0.2	5.2
31.00	0.1	>40	tr	19.2	0.1	0.4	0.1	4.7
46.50	0.2	>40	tr	20.0	0.1	0.4	0.2	5.9
62.00	0.1	>40	0.1	21.1	0.1	0.5	0.2	7.5
77.50	0.1	35	tr	20.5	0.2	0.5	0.3	8.1

* Initial P concentration approximate only; exact concentration calculated from actual soil: solution ratio for each sample. This applies to all Appendix Tables.

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TABLE C-2. EXPERIMENT 2. SUMMARY OF EXPERIMENTAL RESULTS FOR EFFECTS OF REDUCTION ON PHOSPHATE SORPTION ISOTHERMS AT PH 5.0.

Redox potential (mv)	-150	+65	+280	+500
Days of incubation	28	28	26	26
Final pH	35.9	4.5	3.5	2.7

Phosphate Sorption ($\mu\text{g P/g soil}$)

Initial P conc. $\mu\text{g/ml}$	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x
0.03	0.025	29	0.009	76	0.006	37	0.004	28
3.88	0.088	53	0.016	100	0.009	60	0.016	52
7.75	0.250	76	0.050	123	0.060	83	0.067	78
15.50	1.030	119	0.310	169	0.380	128	0.526	126
23.25	2.360	157	1.250	211	1.310	166	1.680	169
31.00	4.390	192	2.810	247	2.860	204	3.590	206
46.50	9.900	253	7.650	312	8.100	266	9.000	265
62.00	16.700	306	14.200	368	15.350	315	17.700	313
77.500	24.100	356			22.500	359	25.800	352

Iron and Manganese Analyses ($\mu\text{g/ml}$)

	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
0.03			6.3	>59	1.5	>50	.5	28
3.88	590	49	5.1		0.3		.2	
7.75	590	51	3.0		0.3		.2	
15.50	600	52	3.8		1.5		.2	
23.25	550	50	5.6	>50	0.3	>50	.2	
31.00	550	50	6.1		0.5		.2	
46.50	530	52	5.5		0.3		.3	
62.00	520	54	3.0	>50	0.2		.2	
77.50	525	48				>50	.2	21

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TABLE C-3. EXPERIMENT 2. SUMMARY OF EXPERIMENTAL RESULTS FOR EFFECTS OF REDUCTION ON PHOSPHATE SORPTION ISOTHERMS AT PH 6.5.

Redox potential (mv)	-150	+65	+280	+500
Days of incubation	27	26	24	25
HCl added (ml)	2.0			
NaOH added (ml)		3.1	4.6	4.3

Phosphate Sorption ($\mu\text{g P/g soil}$)

Initial P conc. $\mu\text{g/ml}$	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x
0.03	0.017	255	0.004	40	0.002	30	0.006	18
3.88	0.019	280	0.019	64	0.030	56	0.026	41
7.75	0.030	305	0.090	87	0.110	77	0.108	65
15.50	0.032	353	0.495	130	0.684	120	0.585	108
23.25	0.051	401	1.270	172	1.730	161	1.670	147
31.00	0.087	446	3.010	207	3.430	198	3.280	183
46.50	0.327	527	7.670	268	8.750	259	8.680	244
62.00	0.820	611	13.600	325	16.300	308	16.400	293
77.50	1.020	712	21.600	360	25.300	343	25.900	327

Iron and Manganese Analyses ($\mu\text{g/ml}$)

	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
0.03	0	>40	0	14	0	0	0	0
3.88	0	38	0	12	0	tr	0	0
7.75	0	34	0	12	0	0	0	0
15.50	0	36	0	13	0	0	0	0
23.25	0.2	39	0	13	0	tr	0	0
31.00	0	34	0	13	0	0	0	0
46.50	0.2	35	0	13	0	0	0	0
62.00	2.5	37	0	13	0	tr	0	0
77.50	0	30	0	14	0	0	0	0

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TABLE C-4. EXPERIMENT 2. SUMMARY OF EXPERIMENTAL RESULTS FOR EFFECTS OF
REDUCTION ON PHOSPHATE SORPTION ISOTHERMS AT PH 8.0.

Redox potential (mv)	-150	+65	+500
Days of incubation	28	28	27
NaOH added (ml)	21.3	16.0	23.1

Phosphate Sorption (µg P/g soil)

Initial P conc. µg/ml	c	x	c	x	c	x
0.03	0.016	17	0.006	8	0.010	12
3.88			0.049	32	0.097	35
7.75	0.183	64	0.205	54	0.310	58
15.50	0.647	109	0.826	98	1.030	100
23.25	1.360	152	1.410	142	2.000	142
31.00	2.100	196	2.220	184	2.930	184
46.50	3.480	283	4.420	268	5.330	264
62.00	5.470	364	6.930	345	7.850	340
77.50	7.400	446	10.600	418	11.450	410
124.00	17.450	669				

Calcium and Manganese Analyses (µg/ml)

	Ca	Mn	Ca	Mn	Ca	Mn
0.03	182	2.2	173	2.2	115	0
3.88			170	1.9	118	0
7.75	187	1.9	167	1.7	110	0
15.50	190	1.8	173	1.9	101	0
23.25	184	1.8	166	2.2	108	0
31.00	172	1.9	159	2.3	100	0
46.50	164	1.9	138	2.3	86	0
62.00	155	1.9	138	2.5	81	0
77.50	150	1.8	127	2.5	68	0
124.0	113	1.7				

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TABLE C-5. EXPERIMENT 2. EFFECTS OF PHOSPHATE SORPTION REACTIONS ON PH OF REDUCED SOIL SUSPENSIONS

Redox potential (mv)	-150	+65	+280	+500
Controlled pH	5.0	5.0	5.0	5.0
Initial P conc. (µg/ml)				
3.88	5.3	4.8	4.8	4.9
7.75	5.3	4.8	4.8	4.9
15.50	5.0	4.8	4.7	4.8
23.25	4.8	4.8	4.7	4.8
31.00	4.8	4.7	4.7	4.8
46.50	4.7	4.7	4.6	4.8
62.00	4.6	4.7	4.6	4.8
77.50	4.5	4.7	4.6	4.7
Controlled pH	6.5	6.5	6.5	6.5
Initial P conc. (µg/ml)				
7.75		5.8	6.4	6.3
15.50	5.2	5.6	6.3	6.2
23.25	5.2	5.5	6.3	6.1
31.00	5.1	5.4	6.2	6.1
46.50	5.2	6.0	6.1	6.0
62.00	5.3	6.2	6.1	5.9
77.50	5.3	6.2	6.0	5.9
Controlled pH	8.0	8.0		8.0
Initial P conc. (µg/ml)				
0.03				8.0
3.88				7.9
7.75	7.3	7.5		7.8
15.50	7.3	7.5		7.7
23.25	7.2	7.5		7.7
31.00	7.2	7.5		7.6
46.50	7.1	7.4		7.6
62.00	7.1	7.3		7.5
77.50	7.0	7.2		7.4

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TABLE C-6. EXPERIMENT 3. SUMMARY OF EXPERIMENTAL RESULTS FOR EFFECTS OF
RE-OXIDATION ON PHOSPHATE SORPTION ISOTHERMS AT PH 5.5

Redox potential (mv)			
initial	-150	+65	+500
final	+470	+570	+570
Days of incubation			
	21	21	24
pH: initial			
	6.6	5.9	5.2
final			
	5.5	5.5	5.5

Phosphate Sorption ($\mu\text{g P/g soil}$)

Initial P conc. $\mu\text{g/ml}$	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x
0.03	0.020	71	0.014	37	0.006	32
3.88	0.042	96	0.042	60	0.048	57
7.75	0.120	121	0.209	84	0.200	80
15.50	0.600	168	1.080	126	1.030	124
23.25	1.580	211	2.580	165	2.660	163
31.00	3.250	250	4.920	199	4.960	197
46.50	8.550	317	11.700	251	12.000	250
62.00	15.400	375	19.900	296	21.000	290
77.50	24.200	415	30.400	326	30.500	327

Iron and Manganese Analyses ($\mu\text{g/ml}$)

	Fe	Mn	Fe	Mn	Fe	Mn
0.03	tr	>40	tr	0.4	0.2	0.4
3.88	tr	>40	tr	tr	0.2	0.1
7.75	tr	>40	tr	tr	0.1	0.1
15.50	tr	>40	tr	tr	0.2	0.2
23.25	tr	>40	tr	tr	0.1	0.2
31.00	tr	>40	tr	0.1	0.2	0.1
46.50	tr	>40	tr	0.1	0.4	0.1
62.00	tr	>40	tr	0.1	0.2	0.1
77.50	tr	>40	tr	0.1	0.2	0.1

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TABLE C-7. EXPERIMENT 3. SUMMARY OF EXPERIMENTAL RESULTS FOR EFFECTS OF
RE-OXIDATION ON PHOSPHATE SORPTION ISOTHERMS AT PH 5.0

Redox potential (mv)

initial	-150	+65	+280	+500
final	500	530	550	560
Days of incubation	20	20	21	21
NaOH added (ml)	9.0	0.5	0.5	0.3

Phosphate Sorption ($\mu\text{g P/g soil}$)

Initial P conc. $\mu\text{g/ml}$	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x
0.03	0.014	250	0.009	50	0.007	50	0.006	50
3.88	0.019	274	0.050	72	0.026	76	0.023	76
7.75	0.029	299	0.210	94	0.114	101	0.125	101
15.50	0.083	346	0.990	134	0.715	148	0.692	148
23.25	0.152	393	2.800	169	2.050	190	1.970	190
31.00	0.281	440	5.260	199	4.200	227	3.920	228
46.50	0.840	531	12.900	245	9.650	292	10.300	288
62.00	2.280	614	21.300	286	17.800	338	18.000	337
77.50	4.900	691	31.900	319			28.300	371

Iron and Manganese Analyses ($\mu\text{g/ml}$)

	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
0.03	0.2	>40	0.2	43	tr	19	tr	15
3.88	0.2		tr		tr		tr	
7.75	0.2		tr		tr		tr	
15.50	0.2		tr		tr		tr	
23.25	0.2	>40	tr	23	tr	13	tr	11
31.00	0.2		tr		tr		tr	
46.50	0.3		tr		tr		0	
62.00	0.2		tr		tr		tr	
77.50	tr	>40	tr	20	tr	12	tr	10

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TABLE C-8. EXPERIMENT 3. SUMMARY OF EXPERIMENTAL RESULTS FOR EFFECTS OF RE-OXIDATION ON PHOSPHATE SORPTION ISOTHERMS AT PH 6.5

Redox potential (mv)

initial	-150	+65	+200	+500
final	580	580	580	580
Days of incubation	27	27	28	27
NaOH added (ml)	2.6	1.1	0.5	0.6

Phosphate Sorption ($\mu\text{g P/g soil}$)

Initial P conc. $\mu\text{g/ml}$	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x
0.03	0.007	16	0.008	16	0.004	12	0.002	5
3.88	0.048	39	0.090	39	0.053	36	0.068	29
7.75	0.236	62	0.384	60	0.230	58	0.281	53
15.50	1.050	103	1.610	98	1.080	106	1.200	96
23.25	2.530	140	3.780	130	2.850	136	3.000	135
31.00	4.700	172	6.630	157	5.080	170	5.530	168
46.50	11.150	227	14.300	201	11.850	221	12.500	221
62.00	19.300	266	24.100	231	19.400	264	21.300	266
77.50	27.400	293	30.700	249	29.700	294	30.100	295

Iron and Manganese Analyses ($\mu\text{g/ml}$)

	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
0.03 - 77.50	0	0.1-0.2	0	0.1-0.2	0	0	0	0

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TABLE C-9. EXPERIMENT 3. SUMMARY OF EXPERIMENTAL RESULTS FOR EFFECTS OF
RE-OXIDATION ON PHOSPHATE SORPTION ISOTHERMS AT PH 8.0

Redox potential (mv)			
initial	-150	+65	+500
final	+500	+505	+515
Days of incubation	25	24	24
NaOH added (ml)	2.2	1.8	0.7

Phosphate Sorption ($\mu\text{g P/g soil}$)

Initial P conc. $\mu\text{g/ml}$	$\mu\text{g/ml}$	x	$\mu\text{g/ml}$	x	$\mu\text{g/ml}$	x
0.03	0.070	13	0.030	14	0.040	21
3.88	0.523	35	0.315	36	0.420	42
7.75	1.220	56	0.880	57	1.110	62
15.50	2.570	98	2.100	97	2.630	100
23.25	3.730	141	3.680	135	4.000	139
31.00	5.040	185	5.100	173	5.400	176
46.50	7.930	271	8.600	245	9.000	245
62.00	11.400	351	12.400	315	12.700	309
77.50	15.800	416	17.500	370	17.500	369

Calcium and Magnesium Analyses ($\mu\text{g/ml}$)

	Ca	Mg	Ca	Mg	Ca	Mn
0.03	97	14	130	17	85	15
3.88	100	15	136	17	102	16
7.75	79	15	116	17	84	15
15.50	83	15	114	17	81	15
23.25	77	15	99	17	86	15
31.00	75	15	96	17	88	15
46.50	65	15	98	17	75	15
62.00	66	14	88	17	71	15
77.50	60	14	77	17	61	15

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TABLE C-10. EXPERIMENT 4. SUMMARY OF EXPERIMENTAL RESULTS FOR EFFECTS OF DURATION OF ANAEROBIOSIS ON PHOSPHATE SORPTION AT PH 6.5

Redox potential (mv)	-150	-150	-150	-150
Time (days)	1	6	9	18
NaOH added (ml)	2.4	1.9	2.3	
HCl added (ml)				1.7

Phosphate Sorption ($\mu\text{g P/g soil}$)

Initial P conc. $\mu\text{g/ml}$	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x
0.03	0.004	35	0.003	31	0.002	24	0.001	5
3.38	0.015	60	0.012	56	0.012	36	0.019	28
7.75	0.026	85	0.024	81	0.022	59	0.037	51
15.50	0.091	132	0.104	129	0.110	106	0.315	95
23.25	0.210	178	0.198	176	0.403	151	0.554	140
31.00	0.430	222	0.490	222	0.720	195	0.970	183
46.50	1.340	311	1.710	309	2.350	278	3.820	260
62.00	3.290	393	3.820	388	5.340	352		
77.50	6.100	464	7.050	455	9.250	418	12.000	392

Iron and Manganese Analyses ($\mu\text{g/ml}$)

Initial P conc. $\mu\text{g/ml}$	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
0.03	0.3	14	17	26	11	36	18	NM
3.88	0.5	14	15	23	8	22	35	
7.75	0.5	14	16	23	9	22	33	
15.50	0.7	15	18	22	8	21	43	
23.25	1.0	15	17	22	11	20	35	
31.00	1.4	14	18	22	12	20	26	
46.50	1.5	14	19	21	14	19	45	
62.00	2.1	14	20	20	14	18	46	
77.5	2.5	14	20	19	11	18	39	

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TABLE C-11. EXPERIMENT 4. SUMMARY OF EXPERIMENTAL RESULTS FOR EFFECTS OF DURATION OF PRIOR ANAEROBIOSIS AND SUBSEQUENT RE-OXIDATION ON PHOSPHATE SORPTION ISOTHERMS AT PH 5.5

Redox potential (mv)				
anaerobic	-90	-150	-150	-150
aerobic	530	490	525	500
Time (days)				
anaerobic	1	6	9	18
aerobic	20	26	26	25
NaOH added (n.l)			0.1	1.3

Phosphate Sorption ($\mu\text{g P/g soil}$)

Initial P conc. $\mu\text{g/ml}$	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x	c $\mu\text{g/ml}$	x
0.03	0.011	72	0.008	56	0.003	11	0.039	10
3.88	0.035	97	0.021	79	0.043	35	0.070	33
7.75	0.133	121	0.113	102	0.196	57	0.184	55
15.50	0.700	167	0.620	146	0.970	100	0.840	95
23.25	1.900	209	1.730	186	2.420	138	2.250	130
31.00	3.820	248	3.330	223	4.660	170	4.400	159
46.50	9.370	310	9.600	279	11.200	225	9.900	211
62.00	16.500	364	15.700	336	20.100	265	17.900	247
77.50	26.700	399	24.700	373	27.900	311	26.300	271

Iron and Manganese Analyses ($\mu\text{g/ml}$)

	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
0.03 - 77.50	0.1	22-26	0	0.1-0.3	0-0.2	0.5-0.5	0	0.5-0.9

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APPENDIX D

TABLE D-1. REDOX POTENTIAL (MV) VALUES MEASURED AT VARIOUS DEPTHS DURING OVERLAND FLOW TREATMENT OF SIMULATED WASTEWATER IN CROWLEY SOIL-RYE GRASS SYSTEM*

Days	Soil pretreatment								
	untreated			prereduced			limed		
	soil depth, cm			soil depth, cm			soil depth, cm		
	0.5	3.0	6.0	0.5	3.0	6.0	0.5	3.0	6.0
1**	562	592	537	500	530	525	492	542	562
2	495	522	507	450	468	500	460	442	467
3	407	542	422	450	400	430	397	372	367
4	410	337	372	392	340	340	377	332	347
5	359	317	329	370	300	320	362	312	317
8*	579	567	559	500	520	523	520	507	404
9	465	437	332	470	410	340	457	367	377
10	402	282	304	390	300	290	447	322	322
11	465	282	362	395	295	308	430	357	350
12	344	177	495	350	240	350	414	302	340
15**	637	667	562	600	590	540	530	537	550
16	495	462	312	510	440	350	502	477	547
17	400	277	240	390	310	280	500	432	530
18	382	82	160	370	200	310	504	447	550
19	380	47	165	350	100	180	502	457	545
22**	627	687	667	590	602	620	562	547	597
23	377	307	360	400	300	335	540	517	547
24	252	22	262	280	30	242	480	287	245
25	222	32	290	290	20	240	487	287	452
26	140	170	220	200	50	200	460	267	402
29	542	652	542	565	580	500	510	442	547
30	617	702	588	580	600	520	522	527	562
31	Plants harvested								
33	Soil mass sectioned								

* Data reported are averages of two platinum electrode readings corrected for reference electrode potential.

** Simulated wastewater applied after a 2-day break.

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TABLE D-2. RECOVERY OF APPLIED PHOSPHORUS-32 IN THE COMBINED RUNOFF PLUS SUBFLOW EFFLUENT DURING AN OVERLAND FLOW TREATMENT OF SIMULATED WASTEWATER IN CROWLEY SOIL-RYE GRASS SYSTEM ESTABLISHED ON 1.2% SLOPE*

Application number	Treatments		
	untreated	prereduced	limed
	³² P recovered, %		
1 + 2	16.01	4.84	1.36
3	23.56	8.36	5.28
4	28.28	11.02	6.47
5	25.42	9.86	3.14
6**	18.75	6.78	1.27
7	36.51	17.86	6.45
8	29.38	18.06	5.40
9	33.00	19.54	5.35
10	30.57	16.38	1.70
11**	24.22	9.39	0.38
12	40.58	25.36	4.90
13	40.04	24.08	5.17
14	48.04	25.90	4.19
15	38.25	26.46	3.78
16**	48.00	20.34	0.48
17	60.82	25.35	1.59
18	36.44	21.26	1.00
19	46.78	25.04	1.70
20	33.62	20.82	1.38
Grand Average	34.65	18.25	3.21

* Data reported are average of two replications.

** Simulated wastewater applied after a 2-day break.

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TABLE D-3. VOLUME OF SIMULATED WASTEWATER RECOVERED IN THE COMBINED RUNOFF PLUS SUBFLOW EFFLUENT DURING AN OVERLAND FLOW TREATMENT OF WASTEWATER IN CROWLEY SOIL-RYE GRASS SYSTEM ESTABLISHED ON 1.2% SLOPE*

Application number	Treatments		
	untreated	prereduced	limed
	Volume recovered, ml		
1 + 2	1073	1022	759
3	760	571	662
4	788	744	699
5	792	735	672
6**	489	383	269
7	794	761	680
8	791	745	683
9	801	750	693
10	770	714	651
11**	491	361	181
12	715	745	631
13	797	748	666
14	823	754	725
15	729	719	639
16**	513	356	280
17	729	673	612
18	560	580	489
19	674	676	615
20	506	601	483

* Data reported are average of two replications.

** Simulated wastewater applied after a 2-day break.

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TABLE D-4. pH VALUES OF 1:5 SOIL- 0.01M CALCIUM CHLORIDE EXTRACTS OF CROWLEY SOIL SAMPLES COLLECTED AT THE END OF OVERLAND FLOW EXPERIMENT*

Distance downslope, cm	Soil depth, cm	Treatments		
		untreated	prereduced	limed
0-25	0-2	6.1	6.6	7.2
	2-4	6.2	6.5	7.3
	4-8	6.1	6.5	7.4
25-50	0-2	6.3	6.6	7.5
	2-4	6.3	6.7	7.7
	4-8	6.0	6.5	7.5
50-75	0-2	6.1	6.7	7.6
	2-4	6.1	6.7	7.7
	4-8	6.0	6.9	7.7
75-100	0-2	6.3	6.9	7.7
	2-4	6.2	6.9	7.7
	4-8	6.1	6.7	7.7

* Data reported are averages of two replications.

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TABLE D-5. CONCENTRATIONS OF APPLIED SOLUBLE PHOSPHORUS, PHOSPHORUS REMAINING IN SOLUTIONS AFTER 24 HOURS EQUILIBRATION AND PHOSPHORUS SORBED BY SOIL COMPLEX IN VARIOUS SOIL PRETREATMENTS IN CROWLEY SOIL DETERMINED IN THE LABORATORY*

P applied μg/ml	Treatments					
	untreated soil		prereduced		limed	
	solution P	sorbed P	solution P	sorbed P	solution P	sorbed P
	μg/ml	μg/g	μg/ml	μg/g	μg/ml	μg/g
0	0.01	—	0.01	—	0.03	—
5	0.02	24.9	0.02	24.9	0.06	24.7
10	0.05	49.7	0.03	49.8	0.11	49.4
20	0.15	99.2	0.14	99.3	0.32	98.4
30	0.60	147.0	0.32	148.4	0.72	146.4
40	1.81	193.9	0.67	196.6	1.40	193.0
60	4.17	279.1	2.42	287.9	3.82	280.9
80	9.70	351.5	4.72	376.4	7.16	364.2
100	18.82	405.9	10.96	445.2	12.38	438.1

* Sorption isotherms determined in 1:5 soil - 0.01 M calcium chloride ratio.

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